SANDIA REPORT

SAND89—2106 • UC—706
Unlimited Release
Printed February 1990

AD-A222 100

Moisture Control in Sealed Electronic Packages

M. R. Keenan

DTIC
ELECTE
MAY 24 1990
S B D

SF2900Q(8-81)

90 05 23 028

REPORT DOCUMENTATION PAGE

1 AGENCY USE ONLY (Leave blank)	2 REPORT DATE	3 REPORT TYPE AND DATES COVERED
	May 90	FINAL FEB 89 - MAR 90

4 TITLE AND SUBTITLE	5 FUNDING NUMBERS
MOISTURE CONTROL IN SEALED ELECTRONIC PACKAGES	25020838

6 AUTHOR(S)

M. R. KEENAN

AFATL Program Manager: Steven Smith (MNF)

7 PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8 PERFORMING ORGANIZATION REPORT NUMBER
SANDIA NATIONAL LABORATORIES ALBUQUERQUE, NEW MEXICO 87185	SAND89-2106

9 SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10 SPONSORING/MONITORING AGENCY REPORT NUMBER
Fuzes and Guns Branch Munitions Division Air Force Armament Laboratory Eglin Air Force Base, FL 32542-5434	AFATL-TP-90-09

11 SUPPLEMENTARY NOTES

This technical paper was not edited by AFATL Technical Reports Section.

12a DISTRIBUTION/AVAILABILITY STATEMENT	12b DISTRIBUTION CODE
Approved for public release; distribution is unlimited.	

13 ABSTRACT (Maximum 200 words)

A number of issues associated with controlling the internal moisture content of sealed packages are examined. The basic strategy for maintaining a dry internal environment is to incorporate desiccant into the package and it is shown that molecular sieves are well suited to this task. Expressions are developed that predict the moisture content of the package in terms of package design and the external storage environment. Both moisture sealed into the package during assembly and water that leaks or permeates into the package over its lifetime are accounted for. In this development, the temperature dependences of all quantities of interest are explicitly treated and the actual Langmuir-like adsorption isotherm exhibited by molecular sieves is employed. These equations allow the quantity of desiccant required to meet design objectives to be computed. They also permit one to evaluate the sensitivity of the internal environment to design parameters and storage conditions, and a number of these are discussed. A computer program that has been written to perform these calculations is also described.

14 SUBJECT TERMS	15 NUMBER OF PAGES
	70
	16 PRICE CODE

17 SECURITY CLASSIFICATION OF REPORT	18 SECURITY CLASSIFICATION OF THIS PAGE	19 SECURITY CLASSIFICATION OF ABSTRACT	20 LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

MOISTURE CONTROL IN SEALED ELECTRONIC PACKAGES*

M. R. Keenan
Sandia National Laboratories
Albuquerque, New Mexico   87185

ABSTRACT

A number of issues associated with controlling the internal moisture content of sealed packages are examined.   The basic strategy for maintaining a dry internal environment is to incorporate desiccant into the package and it is shown that molecular sieves are well suited to this task.   Expressions are developed that predict the moisture content of the package in terms of package design and the external storage environment.   Both moisture sealed into the package during assembly and water that leaks or permeates into the package over its lifetime are accounted for.   In this development, the temperature dependences of all quantities of interest are explicitly treated and the actual Langmuir-like adsorption isotherm exhibited by molecular sieves is employed.   These equations allow the quantity of desiccant required to meet design objectives to be computed.   They also permit one to evaluate the sensitivity of the internal environment to design parameters and storage conditions, and a number of these are discussed.   A computer program that has been written to perform these calculations is also described.

Table of Contents

INTRODUCTION

The long-term reliability of packaged electronic assemblies can be degraded by the presence of large quantities of moisture within the package. Water, by itself and in conjunction with ionic impurities, promotes a number of deleterious processes that can lead to component failure.[1] One obvious problem, if sufficient water is present to support conduction, is short circuiting. Electrochemical corrosion is another major problem that can compromise the integrity of conductors, solder joints, bonds, etc. A related phenomenon in continuously powered circuits is dendritic growth[2] which can quickly produce conductive bridges between conductors on printed circuit boards. Water is also absorbed by organic materials in the package and, as a consequence, may change the mechanical and dielectric properties of circuit boards, encapsulants and other insulating materials. High concentrations of water may also have indirect effects. Water, for example, might react with materials in the package to generate hydrogen which itself can degrade some electronic components.[1]

The key to avoiding these problems is to ensure that the interior of the package remains "dry" over the duration of its life. The conditions that constitute "dry" will be discussed later. For now, it is sufficient to note that we wish to maintain the concentration of water low enough to preclude condensation and to keep surface adsorption below a level that supports ionic conduction.

There are two sources of water that must be accounted for when developing a strategy for moisture control in a package. The first is moisture that is sealed into the package during manufacture. This quantity of water is fixed at assembly time and the moisture may reside in the ambient atmosphere, be adsorbed to free surfaces or dissolved in component materials. Even for hermetically sealed containers, this moisture must be considered. The second source of moisture is leakage or permeation into the package from the external environment. The magnitude of this contribution increases with storage time and depends on the details of the seal design as well as the storage conditions.

The brute force method for controlling moisture consists simply of ensuring that no water is sealed into the package and that none can ever leak in. In fact, this is the approach taken by microcircuit manufacturers who bake out components prior to hermetically sealing in a dry atmosphere. This approach is not feasible. however, for larger packages containing organic materials. In a package containing an epoxy-glass circuit board, for example, bake out times on the order of days to weeks would be required to completely dry out the material. Nor is it always possible or desirable to hermetically seal the package. For reasons of manufacturability, cost or reworkability, large packages are often sealed with elastomeric o-rings or gaskets, adhesives, encapsulants or other organic materials. These seals, while they may not leak in the traditional sense of the word, do allow water to permeate through the bulk of the seal material. Water from permeation is often a major contributor to the total water load that the package will experience.

Rather than limiting the total water content in a package, a second approach to moisture control relies upon sequestering the water in a location that does not degrade the performance of the package. This can be accomplished by adding a desiccant to the package. When properly chosen, the desiccant has a much greater affinity for water than do other materials in the package. As a result, water is preferentially absorbed by the desiccant making it unavailable for surface adsorption or condensation. The moisture control prob-

lem then reduces to defining the amount of desiccant required to accommodate the anticipated water load at a specified level of dryness. As will be shown, zeolite molecular sieves are well suited desiccants for maintaining very low levels of humidity.

The work embodied in this report was conceived in response to a Department of Defense request to support a program to extend the service life of the FMU-139A/B conventional fuze. In this report, I discuss a number of design considerations related to the use of molecular sieve desiccants to control humidity inside of such a sealed package. A model is developed that considers leakage, permeation and the various equilibria that water establishes inside of the package in order to predict the internal environment as function of time and external storage conditions. The model is more realistic than those normally used in this type of calculation since it employs a molecular sieve adsorption isotherm that faithfully reproduces the observed behavior. Using this model, the amount of desiccant required to maintain a specified maximum dew point over the life of the package can be computed. The model can also be used to explore interrelationships among the design parameters and to test the sensitivity of the internal environment to variations in these parameters.

An additional advantage of the model developed here is that it includes explicit temperature dependences for leakage, permeation and internal moisture equilibria. This allows us to address the question of how to deal with a variable external storage environment and an example using a sinusoidally varying storage temperature is presented.

Finally, use of the model is illustrated by computing the desiccant requirements of the FMU-139A/B conventional fuze. A computer program that implements the model is also described.

UNITS USED TO REPRESENT ATMOSPHERIC MOISTURE CONTENT

From the standpoint of reliability, we are primarily concerned with the moisture content in the internal atmosphere of a package since this is the moisture that is readily available for condensation and surface adsorption. Several different quantities can be used to represent this moisture content. A number of these are defined below for future reference.

1. **Mass Density**: This is one absolute way to represent atmospheric moisture content. For a mass M of water in a container having free volume V, the mass density ρ is simply

$$\rho = M/V \tag{1}$$

Convenient units for ρ are $\mu g/cm^3$. Mass density of moisture in air is shown in Fig. 1 as a function of temperature and relative humidity. As can be seen, only small quantities of water are normally present in the atmosphere. If all of the water in one liter of air at 25°C and 50% relative humidity were to be condensed into a single droplet, the volume of the droplet would be only 0.01 ml. a small droplet indeed.

2. **Partial Pressure**: The partial pressure P of water vapor in the atmosphere is the pressure that the water would exert in the absence of any other gases. Within the limits of the ideal gas law, P is related to the mass density of water by

$$P = \rho RT/M_o \qquad (2)$$

where $R = 62363$ torr·cm³/(mole·K) is the gas constant, T is the absolute temperature and $M_o = 18$ gram/mole is the molecular weight of water. In a sealed volume having constant mass density, P increases linearly with T. P will be used extensively in the following model since it conveniently describes the internal moisture equilibria and since leakage and permeation rates are proportional to the partial pressure difference across a seal.
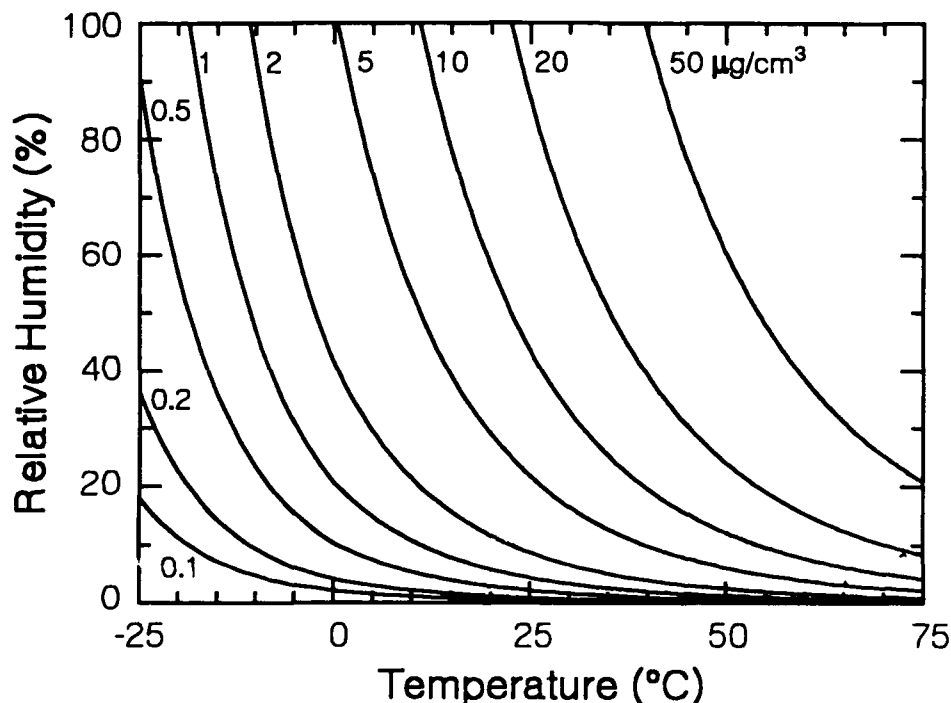
Fig. 1. Mass density of water vapor in the atmosphere. The labeled curves represent lines of constant mass density in $\mu g/cm^3$.

3. **Parts ⊥er Million**: Moisture content in parts per million by volume ppmv expresses the relative concentration of water in the atmosphere. In terms of the partial pressure of water,

$$ppmv = (P/P_T) \times 10^6 \qquad (3)$$

where P_T is the total pressure. The ppmv is effectively the mole fraction of water in the atmosphere. This unit is often used to specify the maximum allowable moisture content inside a package, a practice that can be somewhat misleading. For example, a package sealed at sea level and 25°C and 50% relative humidity will contain 15,700 ppmv of water. The same package sealed under identical conditions in Albuquerque where the atmospheric pressure is only 640 torr will contain 18,600 ppmv of water even though the actual mass of water is the same in both cases. If this unit is to be used in a meaningful way, care must be taken to reference it to a standard pressure, namely, one atmosphere (760 torr).

4. **Relative Humidity**: Relative humidity RH is the ratio of the partial pressure of water vapor to the saturation vapor pressure of water at a given temperature and is normally expressed as a per cent. From Eq. 2,

$$\%RH = \frac{P}{P_S(T)} \times 100 = \frac{\rho RT}{M_o P_S(T)} \times 100 \tag{4}$$

The saturation water vapor pressure $P_s(T)$ is independent of total pressure under the conditions normally encountered in packaging. It is, however, a strong function of temperature[3] as shown in Fig. 2. As a result, RH varies widely with temperature at constant mass density. This is illustrated in Fig. 1. In spite of the large temperature dependence, RH is used extensively in the following model since the extents of surface adsorption and absorption by organic materials are proportional to RH.
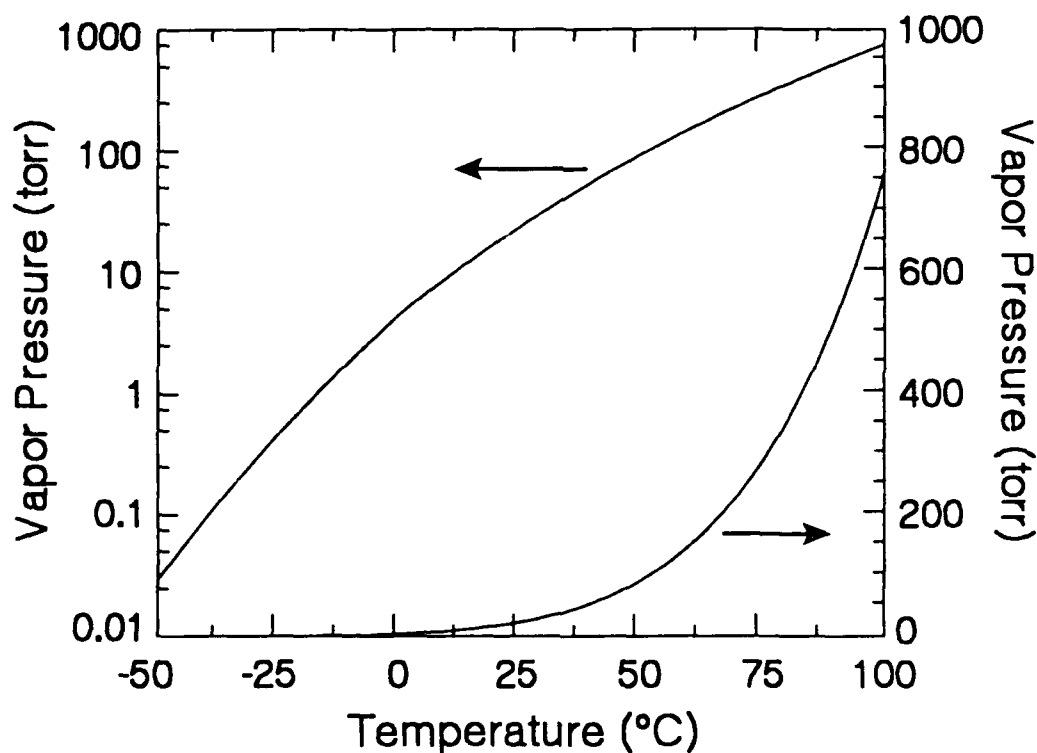
Fig. 2. Saturation pressure of water vapor in the atmosphere. Above 0°C, equilibrium is established with respect to liquid water, and below 0°C, with respect to ice.

5. **Dew Point**: The dew point T_d or frost point T_f is the temperature at which water vapor at a given partial pressure is in equilibrium with the appropriate condensed phase. In other words, at T_d or T_f, air is saturated with water vapor. If air is cooled to or below these temperatures, condensation will occur. T_d or T_f is the inverse function of the saturation pressure described above. As such, it uniquely defines the partial pressure of water vapor in the atmosphere.

One caution that is in order when considering the dew point, is that it is defined with respect to a plane surface of pure water. Owing to the colligative properties of water, the saturation vapor pressure of water will be lowered in the vicinity of ionic contaminants. It will also be lowered in the vicinity of a geometrical feature, such as a crack, where capillary behavior is exhibited.[4] As a result, localized condensation may occur upon cooling before the dew point is reached.

In addition, a couple of subtleties attend the use of dew point in closed systems such as sealed packages. The first is that as a fixed volume of air is cooled, the pressure decreases according to Eq. 2. The result is that T_d or T_f drops with cooling. For example, air at 25°C with a water vapor partial pressure of 0.77 torr has a frost point of -20°C. If the air is then cooled at fixed volume to -20°C, the partial pressure becomes 0.65 torr and the new frost point is -21.8°C. The second subtlety arises from the fact that once condensation begins, the atmosphere loses some of its water thus lowering its partial pressure and dew point. Consequently, progressive cooling is required to condense significant quantities of water.

SPECIFICATION OF MAXIMUM ALLOWABLE MOISTURE CONTENT

There is no universally accepted limit to the maximum permissible amount of moisture that a package ma contain. Indeed, this limit will depend upon factors such as the susceptibility of the particular electronics to moisture related failure, the required level of reliability and packaging costs. In the nuclear weapons community, we have traditionally designed components to meet a -20°C dew point maximum.[5] This standard reflects our desire to maintain a noncondensing environment under normal storage conditions. It is also consistent with the rule of thumb that the internal moisture content should remain below 1000 ppmv for high reliability.[1] It must be emphasized, however, that condensed moisture is neither the only nor primary concern. For example, corrosion and dendritic growth will occur under less than condensing conditions.[6] These processes only require sufficient surface-adsorbed water to support ionic conduction. The extent of surface adsorption is proportional to the ambient relative humidity. From this standpoint, the -20°C dew point requirement appears reasonable since the humidity will be low (≤ 4 %RH) at room and elevated temperatures. In addition, at very low temperatures where the humidity will be high, impeded ionic mobility[7] precludes conduction.

Recently, the use of the dew point to specify maximum allowable moisture content has been criticized.[7,8] The main objection is that the dew point does not adequately reflect the primary role of surface adsorption on moisture induced degradation phenomena. Instead, it is suggested that relative humidity be used to specify water content. In this scheme, however, the humidity as well as the temperature at which it is determined must both be specified. Since moisture content in the atmosphere can be defined equivalently in a variety of units, it is felt here that the dew point can be used adequately as a single figure of merit to specify maximum allowable moisture content. In the remainder of this report, designing to a maximum dew point will be the approach that is taken.

The discussion above pointed out the need to maintain very low levels of atmospheric moisture to ensure the long-term reliability of electronics. This can be achieved by adding desiccants to the package to absorb excess moisture. There are a wide variety of materials that can act as desiccants. These include chemical desiccants such as phosphorus pentoxide, magnesium perchlorate and anhydrous calcium sulfate, and physical adsorbents such as activated alumina, silica gel and zeolite molecular sieves. Clearly, some of these are unsuitable for use in electronic packaging. A good desiccant in this application should be easy to handle, have a high unit absorption capacity for water at very low partial pressures, be chemically inert for high compatibility, have low susceptibility to poisoning and low reversibility if storage conditions are changed. Also, with today's heightened sensitivity toward safety and environmental issues, a good desiccant should be nontoxic and easily disposed of. Based on these considerations, molecular sieve desiccant clearly emerges as the material of choice.

The most common molecular sieve desiccants are based on Type A zeolites. These materials are synthetic aluminosilicates[9] whose crystalline structure[10] contains spherical cavities having a diameter of about 11.4 Å. Access to the cavities is provided through pores whose openings are partially blocked by the cations required to maintain charge neutrality. In Type 4A zeolite, sodium is the counterion and the pore opening is about 4.2 Å in diameter. Type 3A zeolite is a modification of Type 4A in which the pore size is decreased by replacing sodium ions with larger potassium ions. In the case of Type 5A zeolite, two sodium ions are replaced by a single calcium ion to increase the pore size over that of Type 4A. Type 13X zeolite is another popular desiccant that is chemically similar to Type A while having a somewhat different crystal structure. Zeolites selectively adsorb gases and liquids based on molecular size, hence the name molecular sieves. Only molecules that are small enough to pass through the pores of the zeolite can be adsorbed.

Zeolite, as synthesized, is hydrated and its cavities are filled with water. This water can be driven off by heating. The zeolite is then said to be "activated" and the zeolite will rehydrate by adsorbing water from the atmosphere. One of the major advantages of molecular sieves is their high capacity for water at a low concentration of water vapor. In Fig. 3, the adsorption capacity of molecular sieves is compared with that of silica gel and activated alumina as a function of relative humidity.[11] At a dew point of -20°C, the relative humidity is 3-4%. As shown in the figure, molecular sieves have many times the adsorption capacity of the other common desiccants at these low levels of humidity. Adsorption by molecular sieves is also less reversible than that of the other desiccants at temperatures that will normally be encountered in packaging. This is illustrated by the adsorption isobars[12,13] in Fig. 4.
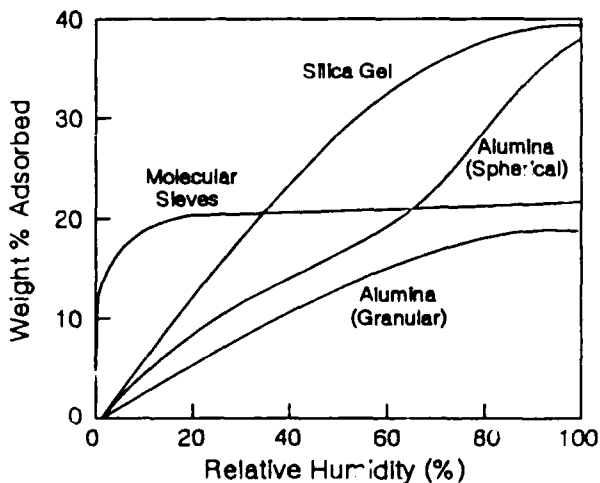
Fig. 3. Adsorption isotherms for some typical desiccants at room temperature. The figure is taken from Ref. 11.
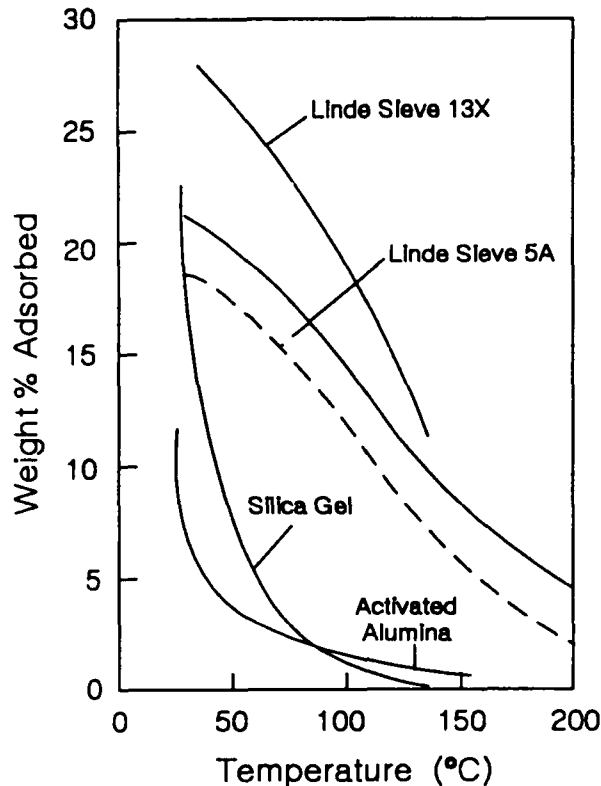
Fig. 4. Moisture adsorption isobars for some typical desiccants. The figure is taken from Ref. 13.

Silica gel and activated alumina rapidly lose capacity as the temperature is raised above 25°C. At 100°C, they have virtually no capacity for water. Molecular sieves, on the other hand, lose less than half of their adsorption capacity as the temperature is raised to 100 °C. Based on this behavior, only molecular sieves will be considered here as being suitable for use in packaging.

The exact choice of molecular sieve depends on the particular application. Type 4A is the best choice for general purpose drying. It has a high adsorption capacity while maintaining good selectivity for water. If greater selectivity toward water is desired, Type 3A can be used although some capacity is sacrificed. In one interesting application, molecular sieves are incorporated into a molding compound. This molded desiccant[12] contains 80% by weight molecular sieves in an epoxy binder. Since the resin system components are relatively large, they are excluded from the molecular sieve and the zeolite retains its theoretical adsorption capacity for water. Other polymers, such as silicone and polyimide, have also served as the matrix material in molded desiccants.

MOISTURE EQUILIBRIA INSIDE OF SEALED PACKAGES

Moisture inside of a sealed package can exist in a number of different states. Water vapor in the atmosphere has already been discussed at length. Moisture may also be adsorbed onto free surfaces in the package, absorbed into materials and bound to a desiccant. At equilibrium, the distribution of water among these states can be conveniently related to the partial pressure of water vapor in the atmosphere. The equilibrium expressions are given below.

1. <u>Mass of water in the atmosphere</u>: The mass of water W_A in the free volume V of a sealed package is obtained from Eqs. 1 and 2

$$W_A = \frac{VM_oP}{RT} \qquad (5)$$

where the symbols have all been previously defined.

2. <u>Mass of water adsorbed to free surfaces</u>: The model for surface adsorption is based on one given in Ref. 8. In this model, the quantity of

water adsorbed to surfaces is proportional to the relative humidity and allows for the build-up of a surface layer of water that is 10 monolayers thick. This model is only approximate and does not take into consideration the nature of the surface. It is adequate for our purposes, however, since in large packages, surface-adsorbed water accounts for only a small portion of the total. The model consists of a linear variation of adsorbed water with relative humidity

$$W_S = K_S A \cdot \%RH/100 \qquad (6)$$

where W_S is the mass of water adsorbed to the surface in grams, K_S is the approximate mass of 10 monolayers of water (3×10^{-7} grams/cm^2) and A is the free surface area in cm^2. Rewriting this in terms of water vapor partial pressure using Eq. 4,

$$W_S = K_S A P/P_S(T) \qquad (7)$$

3. <u>Mass of water absorbed by organic materials</u>: A number of materials, in particular organics, will absorb water into their bulk through a diffusion process.[14] The quantity of water can be significant. Epoxies, for example, absorb as much as a few per cent water by weight at saturation. In general, the total amount of water absorbed is relatively independent of temperature. Rather, it is a function of relative humidity. While the detailed moisture absorption behavior of plastics is very complex, in the model presented here, I will assume that Henry's law is followed and I will disregard any temperature dependence in the Henry's law constant. With these simplifications, moisture absorption becomes directly proportional to the relative humidity. This is a good approximation in the case of hydrophobic polymers such as the polyolefins. For hydrophilic polymers, on the other hand, the saturation absorption tends to increase more rapidly as the humidity is raised. Applying Henry's law in this case will result in a conservative design, when based on the saturation absorption at 100% RH, because the amount of water sealed into the package will be overestimated. Alternatively, a more realistic Henry's law constant can be estimated from the moisture absorption at the humidities of interest.

Given a quantity of material M_i, the mass of water absorbed into the material W_{Mi} is obtained from

$$W_{Mi} = M_i K_i \cdot \%RH/100 \qquad (8)$$

The Henry's law constant K_i is the saturation (100% RH) absorption expressed in grams of water per gram of dry material. If more than one absorbing material is present, it is convenient to define a composite Henry's law constant:

$$K_H = \Sigma M_i K_i / \Sigma M_i = \Sigma M_i K_i / M_M \qquad (9)$$

where M_M is the total mass of organic materials in the package. The total mass of absorbed water then becomes

$$W_M = M_M K_H P/P_S(T) \qquad (10)$$

where %RH has again been expressed in terms of the water vapor partial pressure.

4. **Mass of water adsorbed into molecular sieve desiccant**: The
adsorption of water by molecular sieves follows a Langmuir-like isotherm. A
functional form for this isotherm that reproduces the observed[11] behavior is
given by:

$$S(P) = \frac{nbP}{1 + bP} + c \cdot \ln(1 + P) \qquad (11)$$

S(P) is the equilibrium uptake of the molecular sieves in grams of water per
gram of dry sieve, and n, b and c are constants that depend on the type of
sieve. At 25°C, these constants, derived from the observed isotherm, are:

Type 3A: $n = 0.174$ g_{water}/g_{sieve}, $b = 29.6$ $torr^{-1}$, $c = 0.0138$ g_{water}/g_{sieve}
Type 4A: $n = 0.189$ g_{water}/g_{sieve}, $b = 39.0$ $torr^{-1}$, $c = 0.0116$ g_{water}/g_{sieve}

The actual isotherms[11] are compared with those calculated using Eq. 11 in
Fig. 5 and the agreement is generally quite good.
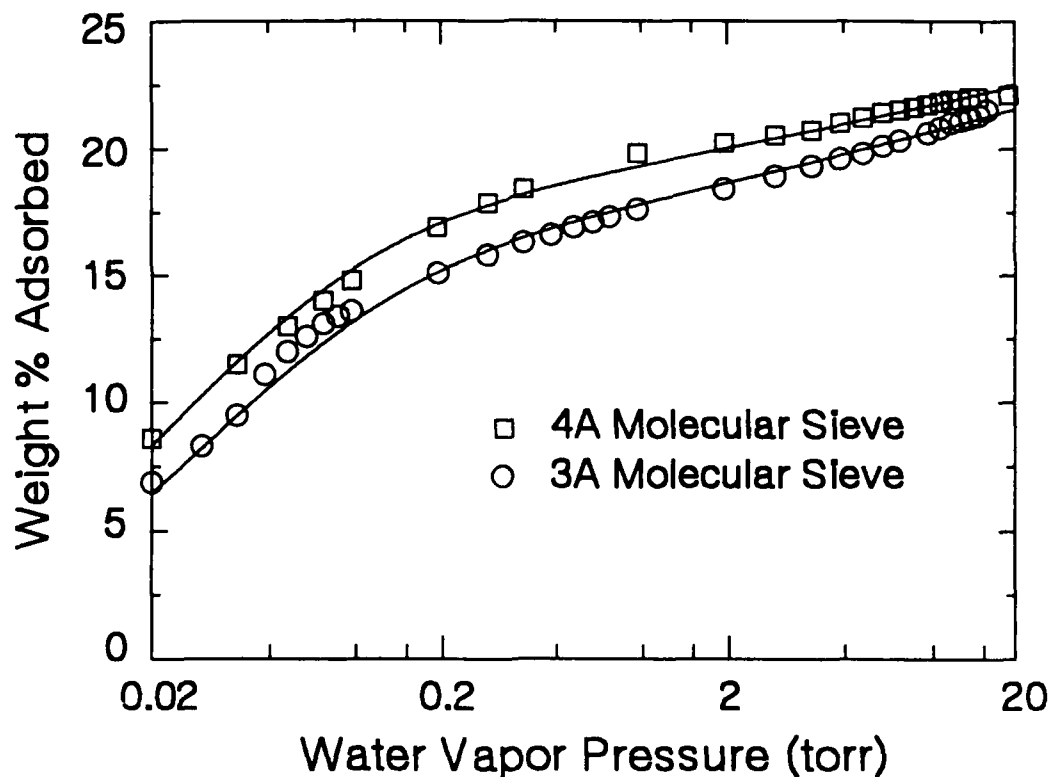
Fig. 5. Comparison of the observed molecular sieve
adsorption isotherms (symbols) with those calculated
using the Langmuir-like function.

As the temperature is changed at constant mass loading, the equilibrium
vapor pressure of water above the molecular sieves varies according to the
Clausius-Clapeyron equation.[13] The vapor pressure P_1 at absolute temperature
T_1 is related to the pressure P_2 at T_2 according to:

$$P_1 = P_2 e^{\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} \qquad (12)$$

where ΔH is the heat of sorption which is approximately 14 kcal/mole[13,15] for molecular sieves and $R = 1.987$ cal/(mole·K). Equation 11 with its associated constants were derived for the adsorption isotherm at 25°C. In order to use this same expression at temperatures other than 25°C, the pressure must be replaced by the equivalent pressure at 25°C as computed from Eq. 12. The most convenient way to do this is to rewrite Eq. 11 as

$$S(P,T) = \frac{nbf(T)P}{1 + bf(T)P} + c \cdot \ln[1 + f(T)P] \qquad (13)$$

with

$$f(T) = e^{\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{298.16}\right]} \qquad (14)$$

Equation 13 can then be used to compute the saturation uptake of the molecular sieves at any temperature and pressure. The total mass of water W_D adsorbed into the molecular sieves in a package is proportional to the mass of sieves M_D according to

$$W_D = M_D S(P,T) \qquad (15)$$

5. **Miscellaneous Water**: Water in a package may be either produced or consumed in chemical reactions. Moisture, for example, is generated during the oxidation of many organic materials and may itself oxidize certain reactive species with the evolution of hydrogen. The quantity of water produced or consumed depends on many factors such as reaction kinetics and the presence of oxygen in the atmosphere. Consideration of these factors and their relationship to the partial pressure of water in the package is well beyond the scope of this report. If, however, these effects are expected and their magnitudes can be estimated, they can be included in the model by assuming that all of this water is instantly available once the package is sealed. This miscellaneous water, the weight of which is denoted W_X, will only be used to help establish the initial equilibria among the four states of water described above.

At equilibrium, the total mass of water in a package $W(P,T)$ is a function of the water vapor partial pressure and temperature and is the sum of the four contributions detailed above:

$$W(P,T) = W_A + W_S + W_M + W_D \qquad (16)$$

or in explicit terms:

$$W(P,T) = \left[\frac{VM_o}{RT} + \frac{K_S A + M_M K_H}{P_S(T)}\right]P + M_D\left[\frac{nbf(T)P}{1 + bf(T)P} + c \cdot \ln[1 + f(T)P]\right] \qquad (17)$$

-12-

Equations 5, 7, 10, 13 and 17 completely specify the equilibrium distribution of water in a package. Given Eq. 17 and any two of the three variables (total mass of water, partial pressure and temperature), the third can be calculated. Once the water vapor partial pressure is known, Eqs. 5, 7, 10 and 15 can be used to compute the mass of water in the atmosphere, on the free surfaces, absorbed in organics and adsorbed by molecular sieves, respectively.

The main use of Eq. 17 will be to calculate the internal water vapor partial pressure given the total quantity of water in a package. Equation 17 can also be employed, however, to estimate the quantity of desiccant needed to dry out an hermetic package. In this case, the total amount of water inside of the package is fixed when the package is sealed and does not change with time. This quantity of water W_o can be computed from Eq. 16 after adding in the contribution from the miscellaneous water:

$$W_o = W_A + W_S + W_M + W_D + W_X = \frac{VM_o P_S(T_S)RH_S}{RT_S} + K_S A RH_S + K_H M_S RH_E + M_D U_D + W_X \quad (18)$$

where T_S and RH_S are the ambient temperature and humidity when the package was sealed, and RH_E is the relative humidity to which the organic materials were equilibrated prior to being sealed into the package. RH_E and RH_S may differ and both are taken as fractions. During the time that the package is being assembled, the molecular sieve desiccant may be exposed to, and adsorb water from, the ambient atmosphere. U_D, in grams of water per gram of desiccant, is the desiccant capacity that is used up in this fashion. Equating Eqs. 17 and 18, and solving for the mass of desiccant gives

$$M_D = \frac{\frac{VM_o}{R}\left[\frac{P_S(T_S)RH_S}{T_S} - \frac{P_S(T_d)}{T}\right] + K_S A\left[RH_S - \frac{P_S(T_d)}{P_S(T)}\right] + K_H M_M\left[RH_E - \frac{P_S(T_d)}{P_S(T)}\right] + W_X}{\frac{nbf(T)P_S(T_d)}{1 + bf(T)P_S(T_d)} + c \cdot \ln[1 + f(T)P_S(T_d)] - U_D} \quad (19)$$

where the partial pressure P has been replaced by the saturation pressure of water vapor at the maximum allowable dew point $P_S(T_d)$. It is interesting to note that the requisite quantity of desiccant is a function of the storage temperature T. Thus, even for hermetic packages, the expected external environment will influence the packaging design.

Up to this point, we have only been concerned with equilibrium conditions and we have not considered the rate that equilibrium is established within a package. In general, equilibrium between moisture in the atmosphere and that adsorbed to free surfaces is essentially instantaneous. Moisture adsorbed to desiccant and absorbed into organic materials, on the other hand, takes a finite amount of time to equilibrate. The time to equilibrium in these cases depends on geometrical factors and material properties such as the diffusion coefficient. As a rule of thumb, equilibration times for molecular sieves will be on the order of hours to days and that for organic materials, days to weeks. For the most part, these times are very short compared to the lifetime of the package and it will be safe to consider all equilibria as being instan-

taneously established. One place where this assumption will lead to an erroneous conclusion will be dealt with later in this report.

LEAKAGE AND PERMEATION INTO A SEALED PACKAGE

After a package is sealed, two mechanisms exist which allow communication between the internal and external atmospheres. Water may leak through channels or cracks. This may be caused, for example, by defects in welds, porosity, or imperfections in o-rings and their sealing surfaces. The other mechanism, when organic materials are used to make the seal, is permeation which results from diffusion through the bulk of the seal material. While the leakage can be minimized by selecting optimum materials and processes, the permeability is a characteristic property of a given organic material and permeation through the material is unavoidable. As a result, packages that utilize organic seal materials cannot be made hermetic.

For both small (molecular) leaks[16] and permeation[17], the flux F of gas through the seal is proportional to the partial pressure difference across the seal

$$F = C(P_E - P) \qquad (20)$$

where C is a conductance and P_E is the external partial pressure. In the case of leakage, the leak size is normally characterized in terms of the helium leak rate and the typical unit for F is atm·cm^3/sec. The unit used for F in the case of permeation, on the other hand, has traditionally been std cc/sec. If the helium leak rate is referenced to standard conditions, then the two units are equivalent. Thus, in this report, I will use std cc/sec to describe both leakage and permeation rates.

The conductance depends on the flow mechanism, geometry of the leak or seal, material properties, temperature and the nature of the gas that is flowing. Expressions for the conductance of water are given below for three particular cases.

1. <u>Leakage with a known helium leak rate</u>: In general, sealed packages are required to pass a leak rate test prior to acceptance. The most common test for packages designed for low leakage is the helium leak check. There are a number of difficulties associated with performing and interpreting these tests, and relating the helium leak rate to that of water. Many of these have been discussed in Refs. 18 and 19, and I will not consider them further here. Rather, I will assume that the helium leak rate accurately reflects the rate that water would flow through the same leak.

The conductance of a molecular leak having a known helium leak rate can be computed from Eq. 20 by realizing that the partial pressure difference during the test is 1 atm (760 torr). From a theoretical standpoint, the conductance involves the average velocity of the gas molecules.[16] This allows us to use the kinetic theory of gases along with the measured helium leak rate to compute the equivalent leak rates for other gases. In the case of water at absolute temperature T, the conductance C_L arising from leakage is given by

$$C_L = \frac{F_{He}}{760}\left(\frac{M_{He}T}{M_o T_o}\right)^{1/2} \frac{\text{std cc}}{\text{sec·torr}} = 0.95 F_{He}\sqrt{T} \frac{\text{grams}}{\text{year·torr}} \qquad (21)$$

$M_{He} = 4$ is the atomic weight of helium and T_0 is the absolute temperature to which the helium leak rate is referenced (273 K). The conductance and leak rate are inversely proportional to the square root of the molecular weight of the leaking gas. Equation 21 is easily generalized to treat other gases, for example argon in place of helium in the leak test, by simply substituting the appropriate values of the molecular weight into the equation.

In the model being developed here, the leak rate is assumed to remain constant over the life of the package and to have the simple temperature dependence outlined above. The reader should be cautioned that this may not prove to be the case in practice. Stress relaxation and aging of organic seal materials can result in a leak rate that increases with time. Also, the temperature dependence of the leak rate may be quite complicated. At cold temperatures, for example, the leak rate may increase due to stiffening of o-ring materials (witness the Challenger disaster) and at elevated temperatures, thermal expansion coefficient mismatches may cause some leaks to seal. While these effects are difficult to predict, the argon analysis approach,[19] which involves gas sampling over the life of a package, can potentially be used to guage the magnitude of these phenomena.

2. _Permeation through a plane_: permeation through an organic polymer is driven by a partial pressure gradient across the material. In the case of a sheet or slab of material having exposed surface area A and thickness ℓ, the steady state flux through the material is given by

$$F_P = AQ(P_E - P)/\ell \qquad (22)$$

where Q is the permeability coefficient for water in the polymer and has the units std cc/(cm·sec·torr). The temperature dependence of the permeability coefficient is given by the Arrhenius expression:

$$Q = Q_0 e^{\frac{-E}{RT}} \qquad (23)$$

where Q_0 and E are the pre-exponential factor and activation energy, respectively. The activation energy for permeation varies widely with material, ranging from slightly negatives values to almost 20 kcal/mole.[14] In general, low permeability materials tend to have higher activation energies. Polystyrene, for example, with a room temperature permeability of 8.4×10^{-9} std cc/(cm·sec·torr) has an activation energy of 0 kcal/mole. Polyvinylidene chloride, on the other hand, whose permeability is 400 times smaller than that of polystyrene has an activation energy of 17.5 kcal/mole.

Substituting Eq. 23 into Eq. 22 and comparing with Eq. 20 shows that the equivalent conductance for permeation through a plane section of material is

$$C_P = \frac{AQ}{\ell} = \frac{A}{\ell} Q_0 e^{\frac{-E}{RT}} \frac{std\ cc}{sec \cdot torr} = 25330 \times \frac{A}{\ell} Q_0 e^{\frac{-E}{RT}} \frac{grams}{year \cdot torr} \qquad (24)$$

In the case where several different materials are employed in sealing the package, the total permeation conductance is simply the sum of the individual conductances. While permeation through a plane is an idealized situation, it

provides a good approximation to permeation through gaskets, adhesive bonds, plastic connectors, plastic containers and encapsulated components.

3. **Permeation through o-rings**: permeation through o-ring seals will be treated as a special case of permeation through a plane. This approach will be examined more thoroughly in Appendix B. For now, it is sufficient to say that this approximation assumes that a compressed o-ring has a rectangular cross section with a cross-sectional area equal to that of the uncompressed o-ring. In this case, the flux of water through an o-ring having a circumference L and compressive sealing strain S is given by[19]

$$F_0 = \left(\frac{4}{\pi}\right) QL(1 - S)^2 (P_E - P) \tag{25}$$

It is interesting to note that the flux through an o-ring seal does not depend on the cross-sectional dimensions of the o-ring but only on the amount of compression used to make the seal. Comparison of Eqs. 20 and 25 shows that the conductance of an o-ring seal is

$$C_0 = \left(\frac{4}{\pi}\right) QL(1 - S)^2 \frac{\text{std cc}}{\text{sec} \cdot \text{torr}} = 32250 \times QL(1 - S)^2 \frac{\text{grams}}{\text{year} \cdot \text{torr}} \tag{26}$$

As before, if a package contains more than one o-ring seal, the total conductance is the sum of the individual conductances. A special situation arises if 2 or more o-rings are employed in series to form a single seal. In this case, the reciprocal conductance of the seal is the sum of the reciprocal conductances of the individual o-rings.

In the cases of both planes and o-rings, permeation is driven by a concentration gradient through the bulk of the material. Before the seal is made, however, these materials are most likely equilibrated with their environment and no concentration gradients exist. The establishment of the concentration gradient after the seal is made can contribute additional water to the interior of the package and it is instructive to examine this transient permeation. For constant concentration boundary conditions, the total quantity of water W_t that has permeated through an unit area of a plane sheet in time t is given by[20]

$$W_t = D(C_1 - C_2)\frac{t}{\ell} + \frac{2\ell}{\pi^2} \sum_{n=1}^{\infty} \frac{C_1 \cos n\pi - C_2}{n^2} \left[1 - e^{-Dn^2\pi^2 t/\ell^2}\right]$$

$$+ \frac{4C_0\ell}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m + 1)^2} \left[1 + e^{-D(2m + 1)^2\pi^2 t/\ell^2}\right] \tag{27}$$

where D is the diffusion coefficient for water in the given organic material. C_1 and C_2 are the concentrations of water just inside of the two surfaces of the sheet and C_0 is the initial concentration of water in the bulk of the

material. These concentrations are related to the water vapor partial pressure through Henry's law (Eq. 8) by

$$C = M_M K_H \cdot \%RH/(100V) \tag{28}$$

where V is the total volume of material. The first term on the right of Eq. 27 represents the water from steady state permeation that was discussed above. The remainder of Eq. 27 is the contribution from transient permeation. Since the steady state will be established quickly relative to the lifetime of a package, we can compute the total water W_{TP} entering the package from transient permeation by setting $t = \infty$ in the last two terms of Eq. 27. Multiplying Eq. 27 by the exposed surface area A, realizing $A\ell = V$, setting $t = \infty$, employing Eq. 28 and evaluating the sums[21] yields

$$W_{TP} = \frac{M_M K_H}{100} \left(\frac{\%RH_E}{2} - \frac{\%RH_S}{6} - \frac{\%RH_I}{3} \right) \tag{29}$$

where $\%RH_S$ is the external storage humidity, $\%RH_I$ is the internal humidity of the package and $\%RH_E$ is the humidity at which the mass M_M of organic material was equilibrated prior to sealing.

To illustrate the magnitude of this effect, consider a package that is internally dry ($\%RH_I = 0$) and whose seal material was equilibrated at the storage humidity ($\%RH_E = \%RH_S$). $W_{TP} = M_M K_H \cdot \%RH_E/300$ or one third of the water initially dissolved in the material will find its way to the package interior. For high permeability and/or low solubility plastics, transient permeation will contribute negligibly to the total water load on the package. This may not be true, however, for low permeability, high solubility materials such as epoxy. In Fig. 6, steady state, transient and total permeation through an
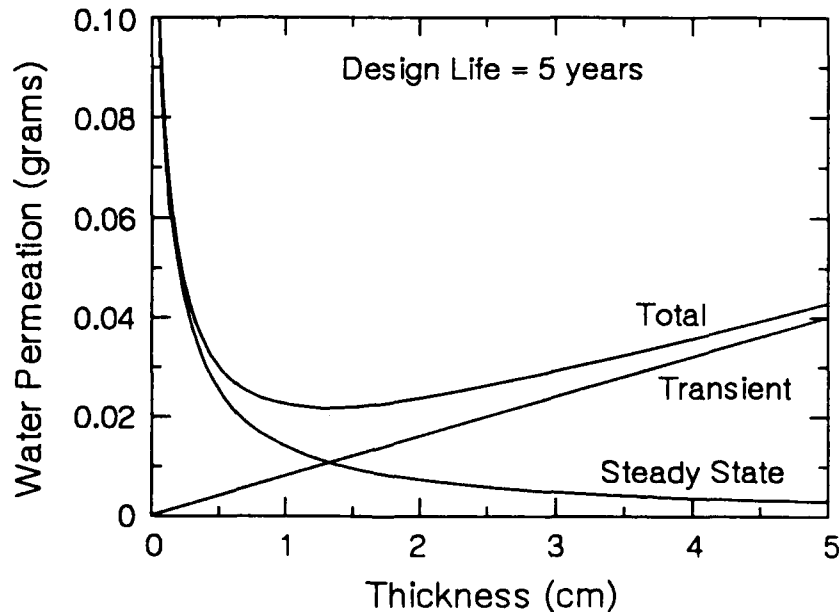
Fig. 6. Steady-state, transient and total permeation through an unit area of a typical epoxy. The fluxes have been integrated over 5 years.

unit area of a typical epoxy[22] are shown as functions of the material thickness for a design life of 5 years. For thicknesses greater than 0.5 cm, transient permeation contributes a significant portion of the total water transported into the package. At the minimum of the curve, the steady-state and transient contributions are equal.

The presence of a minimum in the total permeation curve is explained by noting that steady-state permeation is inversely proportional to thickness while transient permeation increases linearly with thickness. The fact that a minimum exists indicates that the strategy of decreasing permeation by increasing the seal thickness may not always work. The location of the minimum is a function of the design lifetime. This results from the fact that the total transient water is fixed by the initial conditions whereas the total water transported through the seal in the steady state is proportional to time. As the design life increases, steady-state permeation becomes relatively more important. This is illustrated in Fig. 7 for the same epoxy and shows that the optimum seal design, from the standpoint of permeation, must take into consideration the package's operational parameters.
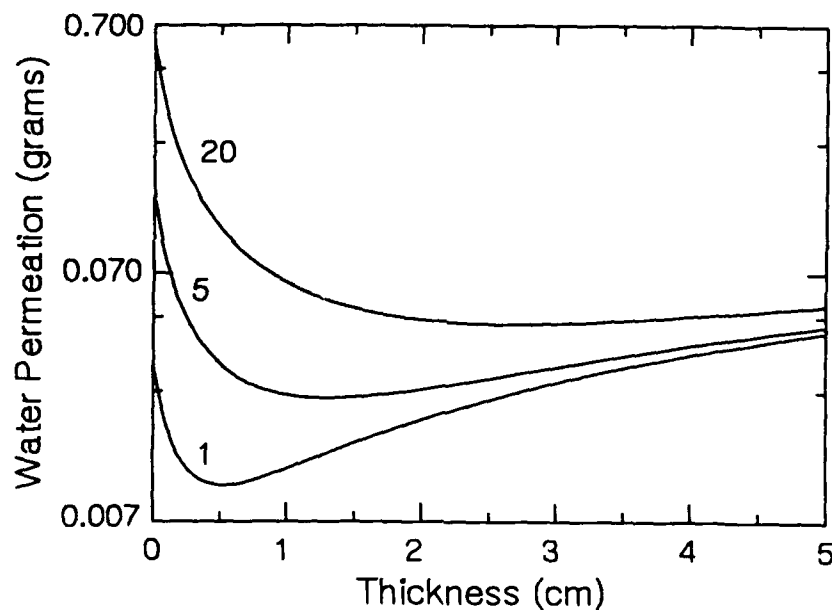
Fig. 7. Total permeation (transient + steady-state) through an unit area of a typical epoxy for different integration times.

Transient permeation could be explicitly incorporated into the model being developed here. This would require, however, the solution of a diffusion equation having time-varying boundary conditions and would lead to unwarranted complexity. Instead, when it is needed, the total water from transient permeation will be computed from Eq. 29 and summed with the miscellaneous water in Eq. 18.

TIME-VARYING MOISTURE CONTENT OF NON-HERMETIC PACKAGES

From the standpoint of electronic reliability, we have been primarily concerned with the atmospheric moisture level inside of a sealed package since this is the water that is readily available for condensation and surface adsorption. For a couple of reasons, the atmospheric moisture content will vary with time. First, leakage and permeation into the package will cause the total water content of the package to increase with storage time. Secondly, variations in the storage temperature will shift the moisture equilibria that are established within the package. This latter effect applies even in the absence of leakage and permeation. Typically, at a fixed total water content, the atmospheric moisture level will increase with temperature. In the packaging design, these variations must be considered when computing the amount of desiccant required to maintain an acceptable internal dew point. In a previous report,[23] the pressure rise in a singly or doubly sealed non-hermetic package containing a Henry's law absorber was computed for isothermal storage conditions. The model developed here will extend that work by relaxing the isothermal storage requirement and by incorporating an adsorption isotherm that more realistically describes the behavior of molecular sieve desiccant.

As shown earlier, the total quantity of water inside of a package is the sum of the water sealed into the package and that which has leaked or permeated into the package during storage. If we assume that equilibration of water within the package is rapid compared to environmental variations and significant leakage or permeation, then the total quantity of water W inside the package is a function of the internal water vapor pressure and storage temperature as shown by Eq. 17. Differentiating W with respect to time and noting that the time rate of change in W is simply the sum of the leakage and permeation rates gives

$$\frac{dW}{dt} = \frac{\partial W}{\partial P}\cdot\frac{dP}{dt} + \frac{\partial W}{\partial T}\cdot\frac{dT}{dt} = (C_L + C_P + C_O)(P_E - P) = C_T(P_E - P) \tag{30}$$

Substituting Eq. 17 for W yields

$$C_T(P_E - P) = \left\{\frac{VM_o}{RT} + \frac{K_S A + M_M K_H}{P_S(T)} + M_D\left(\frac{nbf(T)}{[1 + bf(T)P]^2} + \frac{cf(T)}{1 + f(T)P}\right)\right\}\frac{dP}{dt}$$

$$- \left\{\frac{VM_o}{RT^2} + \left(\frac{K_S A + M_M K_H}{P_S(T)^2}\right)\frac{dP_S(T)}{dT} + \frac{\Delta H M_D}{RT^2}\left(\frac{nbf(T)}{[1 + bf(T)P]^2} + \frac{cf(T)}{1 + f(T)P}\right)\right\} P\frac{dT}{dt} \tag{31}$$

When equilibrium is maintained at each instant, Eq. 31 completely specifies the internal atmospheric moisture content of a package as a function of time and the external storage environment. In the general case, both the storage temperature and humidity may vary with time. If these variations can be described in mathematical terms, Eq. 31 can be solved to give the water vapor partial pressure within a package at all times. Alternatively, Eq. 31 can serve as the basis for calculating the amount of molecular sieve desiccant that should be added to a package to ensure that the internal water vapor

partial pressure will correspond to the maximum allowable dew point at the end of a package's design life.

A number of specific solutions to Eq. 31 will be discussed below. Before treating these, however, a few comments that relate to the general approach to solving this differential equation are in order. The first thing to notice is that Eq. 31 defines an initial value problem. The initial condition, namely, the internal vapor pressure P_0 of water at the time the package is sealed, is calculated from Eqs. 17 and 18 by assuming that equilibrium is established immediately upon sealing.

$$\frac{VM_oP_S(T_S)RH_S}{RT_S} + K_SARH_S + K_HM_SRH_E + M_DU_D + W_X = \qquad (32)$$

$$\left[\frac{VM_o}{RT} + \frac{K_SA + M_MK_H}{P_S(T)}\right]P_0 + M_D\left[\frac{nbf(T)P_0}{1 + bf(T)P_0} + c\cdot\ln[1 + f(T)P_0]\right]$$

Equation 32 is a nonlinear equation in P_0 and must be solved numerically.[24] Once P_0 is computed, Eq. 31 can be readily solved by standard methods (usually numerical) to give the water vapor pressure at any time. Calculation of the amount of desiccant required to control the atmospheric moisture, on the other hand, is a little trickier. This arises from the fact that the initial condition P_0 depends on the amount of desiccant in the package M_D. The strategy for computing M_D, then, is as follows. An initial value of M_D is assumed. P_0 is computed from Eq. 32 and P at the end of the design life is found by solving Eq. 31. If P is greater than the acceptable water vapor partial pressure then M_D is increased and vice versa. The entire procedure is repeated until P equals the partial pressure of water at the specified dew point.

In the work presented here, M_D was adjusted by using the Brent root finding algorithm.[24] This algorithm requires that the root be bracketed prior to entry into the routine. Upper and lower bounds for M_D are easily derived. The lower bound is obtained by assuming that there is neither leakage nor permeation into the package. This is precisely the value of M_D given by Eq. 19. For the upper bound, we wish to maximize the amount of leakage and permeation. This is done by setting P - 0 in Eq. 30. The total mass of water entering the package through leakage and permeation is then C_TP_Et where t is the design life. Adding this quantity of water to the miscellaneous water in Eq. 19 and solving for M_D yields the desired upper bound.

1. <u>Constant storage conditions</u>: when the storage temperature and humidity are constant with time, dT/dt - 0, P_E is a constant, and Eq. 31 can be solved analytically

$$\frac{M_D\,nbf(T)}{1 + bf(T)P_E}\left\{ \frac{bf(T)(P - P_0)}{[1 + bf(T)P][1 + bf(T)P_0]} + \frac{1}{1 + bf(T)P_E}\ln\left[\frac{P_E - P_0}{P_E - P} \cdot \frac{1 + bf(T)P}{1 + bf(T)P_0}\right]\right\}$$

$$\tag{33}$$

$$+\frac{M_D\,cf(T)}{1 + f(T)P_E}\ln\left[\frac{P_E - P_0}{P_E - P} \cdot \frac{1 + f(T)P}{1 + f(T)P_0}\right] + \left[\frac{VM_o}{RT} + \frac{K_S A + M_M K_H}{P_S(T)}\right]\ln\left[\frac{P_E - P_0}{P_E - P}\right] = C_T t$$

This equation is still fairly complex and the numerical methods outlined above must be used to solve for either M_D or P.

At this point, it is interesting to compare and contrast the results derived from Eq. 33 with those obtained from the more approximate methods used in the past. Traditionally, molecular sieve desiccant has been assumed to follow Henry's law and P_0 is taken to be zero. The Henry's law constant K_H' is computed by dividing the equilibrium moisture adsorption of the molecular sieves at a pressure corresponding to the maximum allowable dew point by the humidity at the same pressure

$$K_H' = \left[\frac{nbf(T)P_S(T_d)}{1 + bf(T)P_S(T_d)} + c \cdot \ln[1 + f(T)P_S(T_d)]\right]\frac{P_S(T)}{P_S(T_d)} \tag{34}$$

If we denote the mass of Henry's law molecular sieve by M_D', add $M_D'K_H'$ to the corresponding Henry's law term in Eq. 33, set M_D to zero and solve for M_D', we obtain

$$M_D' = \left\{ \frac{C_T t}{\ln\left[\dfrac{P_E}{P_E - P_S(T_d)}\right]} - \frac{VM_o}{RT} - \frac{K_S A + M_M K_H}{P_S(T)}\right\}\frac{P_S(T)}{K_H'} \tag{35}$$

To put the comparison of Eqs. 33 and 35 on a more concrete basis, consider a hollow cube of polyethylene with an internal volume of 1 liter and a wall thickness of 0.3175 cm (0.125 inch). The package is sealed and stored at 25°C and 50 %RH, and we wish to keep the internal dew point below -20°C for 20 years. The permeability of polyethylene[14] is 9×10^{-10} std cc/(cm•sec•torr). From Eq. 33, the quantity of Type 4A molecular sieve required to meet the design goal is 53.6 grams. Using the simplified approach of Eq. 35, on the other hand, we compute a value of 52.1 grams. These numbers agree quite well and, in general, Eq. 35 could be used to size desiccants for moisture control applications.

The main advantage of using Eq. 33, with its realistic molecular sieve adsorption isotherm, is realized when the package's internal water vapor pressure and dew point are evaluated as functions of time. This is illustrated in Figs. 8 and 9 for the same polyethylene box. At the end of the design life, namely, 20 years, both Eq. 33 and the Henry's law approximation give the same result, a -20°C dew point. The shapes of the two curves, however, differ dramatically. Assuming Henry's law behavior, the internal pressure increases linearly with time and the dew point shows an initial rapid

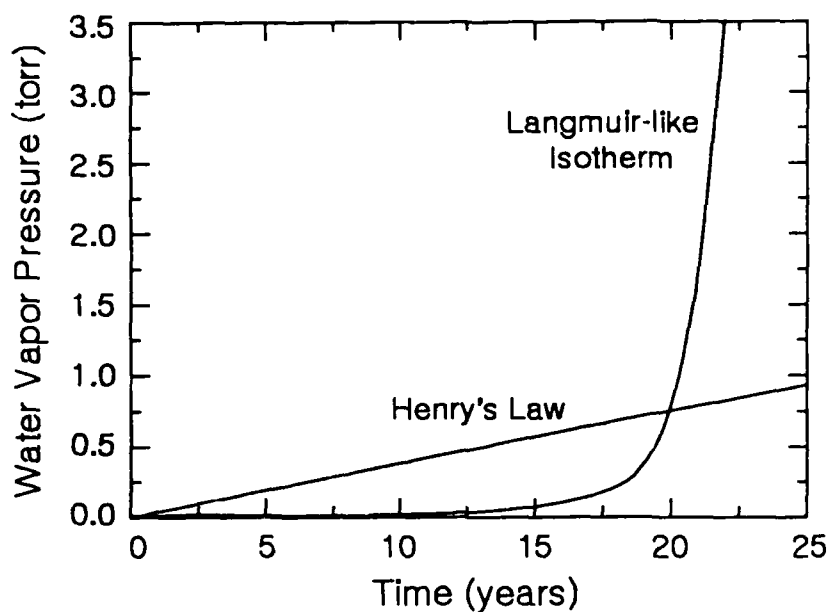Fig. 8. Water vapor partial pressure inside of a polyethylene box as a function of storage time computed using both the Langmuir-like and Henry's law adsorption isotherms.
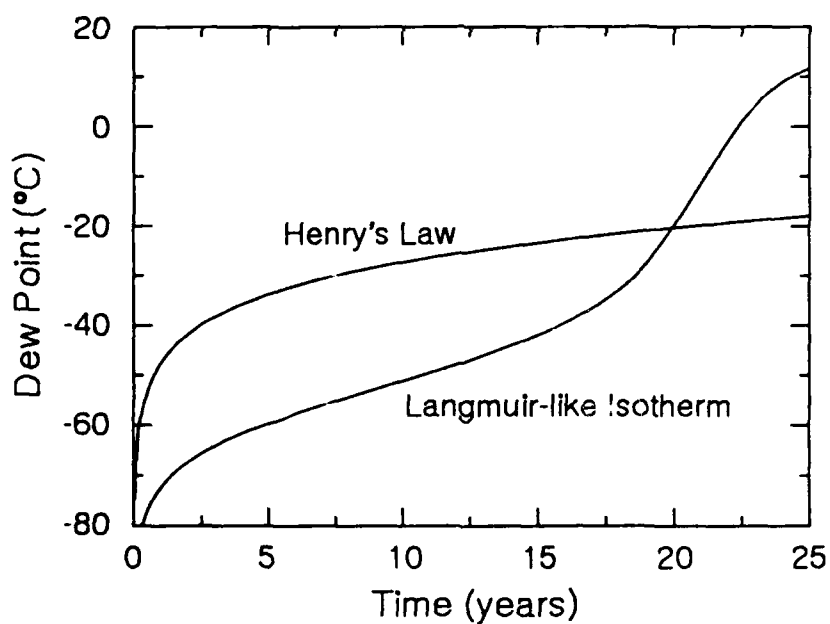
Fig. 9. Dew point inside of a polyethylene box as a function of storage time.

increase after which it gradually reaches and exceeds the specified maximum dew point as the design lifetime is surpassed. The actual behavior will be

opposite to this. In other words, the water vapor pressure and dew point remain relatively low over the bulk of the life of the package but increase very rapidly at the end of the design life.

If the amount of desiccant incorporated in the package is less than that required, the consequences differ drastically in the two cases. In the example given above, if we use only 80% of the estimated quantity of desiccant, then the dew point will exceed -20°C after 16 years in both the Henry's law and Langmuir-like cases. At the end of 20 years, however, the dew point obtained using Henry's law will be only -18°C, whereas, in actuality, the dew point will be 12°C which is nearly equal to that of the external atmosphere. These results suggest that it is especially prudent to design conservatively when using molecular sieves.

Clearly, the supposition that the storage environment remains constant over the duration of a package's lifetime is unrealistic. While the question of variable storage environment will be addressed more fully below, it is appropriate to discuss here one scenario involving a temporary temperature jump. Consider a package that is stored for a length of time at constant temperature and humidity after which the temperature is increased to a higher constant value. The time duration at the higher temperature will be sufficient to re-equilibrate the distribution of water within the package but short enough that the total water mass in the package does not increase significantly through leakage and permeation. In general, the sorptive capacities of the desiccant and organic materials will decrease as the temperature is raised. As a result, the moisture in the internal atmosphere and the dew point will show an increase. If the temperature is now lowered quickly relative to the rate at which the water re-equilibrates to the initial conditions, then moisture will be condensable at much higher temperatures than the initial equilibrium would indicate. This condition is temporary; as the initial equilibrium is re-established, the dew point will return to its original value.

The magnitude of this effect, and the way to counter it, can be derived from the work presented thus far. At the time just prior to the temperature jump, the water vapor partial pressure inside the package can be computed from Eq. 33 and the total water in the package from Eq. 17. Equation 17 can then be solved at the new temperature to yield the re-equilibrated pressure at that elevated temperature. The initial and re-equilibrated dew points are compared in Fig. 10 for the polyethylene box described above. In this example, the size of the temperature jump is 25°C and the dew points are shown as functions of the storage time prior to the jump. Near the end of the design life, the re-equilibrated dew point significantly exceeds the specified maximum dew point. In order to prevent the re-equilibrated dew point from exceeding this maximum, more desiccant will have to be added to the package. The amount of desiccant required can be computed by calculating the total mass of water in the package at the end of the design life from Eq. 33, substituting the water vapor pressure at the maximum allowable dew point $P_S(T_d)$ for P in Eq. 17 and solving Eq. 17 for M_D using the elevated temperature. In the present example, a total of 64.3 grams will be needed to limit the dew point to -20°C. This represents about 20% more desiccant than is required in the absence of a temperature excursion. Of course, the actual increase in desiccant size is a strong function of the size of the temperature jump and details of the package design, and should be evaluated separately for each particular set of circumstances.
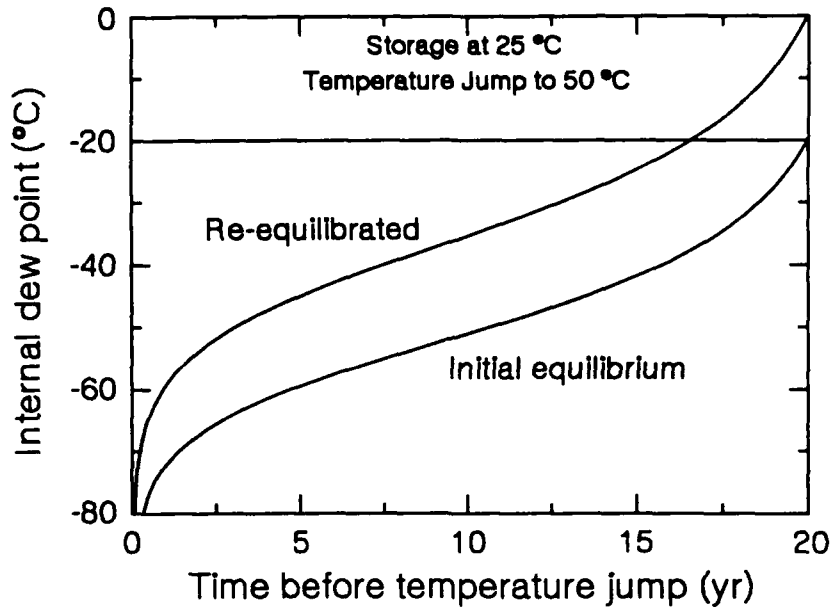
Fig. 10. Using the polyethylene box example pre-
sented in the text, the effect of a temporary storage
temperature jump is demonstrated.

2. **Variable storage temperature**: Typically, the amount of desiccant
required to control moisture in a package is a strong function of the storage
temperature. In general, leakage and, especially, permeation increase while
the sorptive capacities of the desiccant and organic materials decrease with
temperature. This behavior makes it difficult to account for variations in the
storage environment when estimating the proper desiccant size. One approach
is to assume constant storage temperatures and humidities that are equal to
the highest values that are anticipated. While this treatment will certainly
work, it may grossly overestimate the required amount of desiccant. In
Fig. 11, the requisite desiccant size for the polyethylene box example is
shown as a function of storage temperature. The activation energy for the
permeation of water through polyethylene is taken to be 8 kcal/mole[14] and two
specific cases are considered. In the first, the relative humidity is held
constant (external water vapor pressure increases with temperature) and, in
the second, the external water pressure is held constant (relative humidity
decreases with temperature). Both show large increases in desiccant size as
the temperature is increased. In fact, assuming a constant 50 %RH, the poly-
ethylene box requires almost 15 times more desiccant at 50°C than it does at
25°C to maintain a -20°C dew point. Clearly, designing to the expected
environmental extremes may not lead to a practical solution of the temperature
variation problem.

An alternative approach involves solving Eq. 31 which explicitly includes
a term for the variation of storage temperature with time. This approach will
be illustrated for a temperature that varies sinusoidally with time

$$T = T_0 + \Delta T \cos(2\pi t) \qquad \text{and} \qquad \frac{dT}{dt} = -2\pi \Delta T \sin(2\pi t) \qquad (36)$$
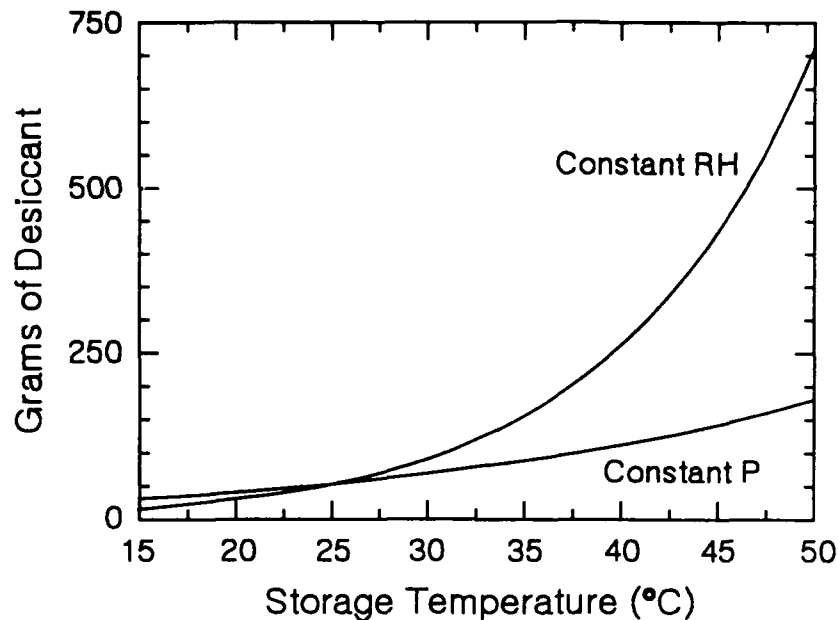
Fig. 11. Quantity of desiccant required to maintain
a -20°C dew point in the polyethylene box example as a
function of the isothermal storage temperature.

T_0 is the average temperature and ΔT is the amplitude of the temperature variation. The period of the sinusoidal temperature variation used here corresponds to an annual cycle. This choice is unimportant as the results will not vary with period if internal equilibrium is maintained at all times. After substituting Eqs. 36 into Eq. 31, M_D can be obtained by using the numerical method described above. The water vapor partial pressure inside the package will vary sinusoidally along with the temperature, but at no point during its design lifetime will the dew point exceed its maximum allowable value. The results obtained for the polyethylene box when subjected to a variable storage temperature are shown by the curves in Fig. 12 for both constant humidity and constant vapor pressure conditions. Once again, the amount of desiccant needed to maintain the desired dew point increases significantly with the maximum storage temperature that the package is exposed to. The amounts, of course, are much less than those obtained by assuming constant storage at the upper temperature and humidity extreme as shown in Fig. 13.

Equation 31 completely describes the effects of a variable storage environment. In practice, however, the use of Eq. 31 is fraught with difficulties. For example, the solution of the equation is very numerically intensive. Using an IBM PC/AT computer equipped with a math coprocessor, about 15 - 20 minutes are required to solve Eq. 31 for M_D with the sinusoidal temperature variation. Also, arbitrary environmental variations are not easily dealt with. In light of these difficulties, it would be desirable to find approximations that would permit the storage temperature to be treated isothermally while giving results that approach those obtained from the full Eq. 31.

One approach is suggested by noting that if the total moisture content inside a package at the end of its design life can be computed, then the quantity of desiccant needed to meet the dew point requirement can be calculated
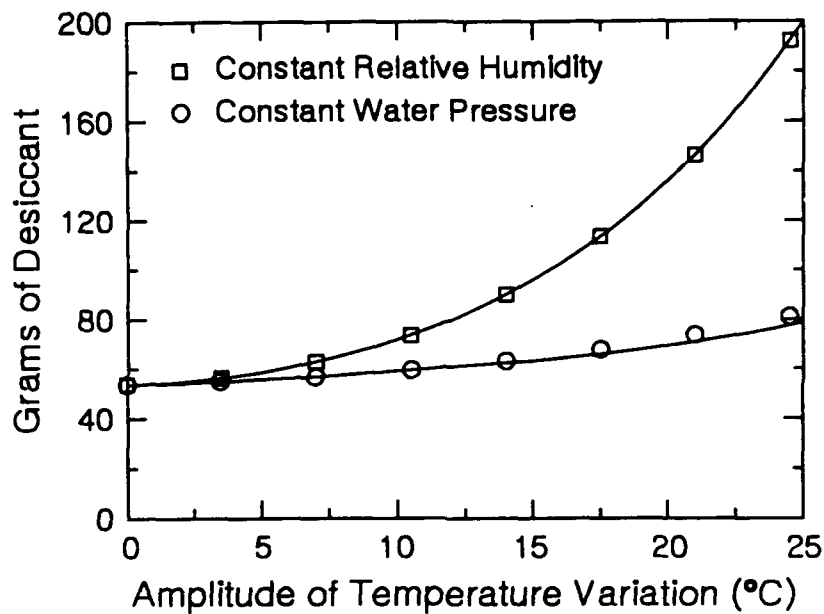
Fig. 12. Effect of a sinusoidally varying storage temperature on the amount of desiccant required to control moisture in the polyethylene box example. The curves were obtained by solving Eq. 31 and the symbols from the approximate method described in the text.
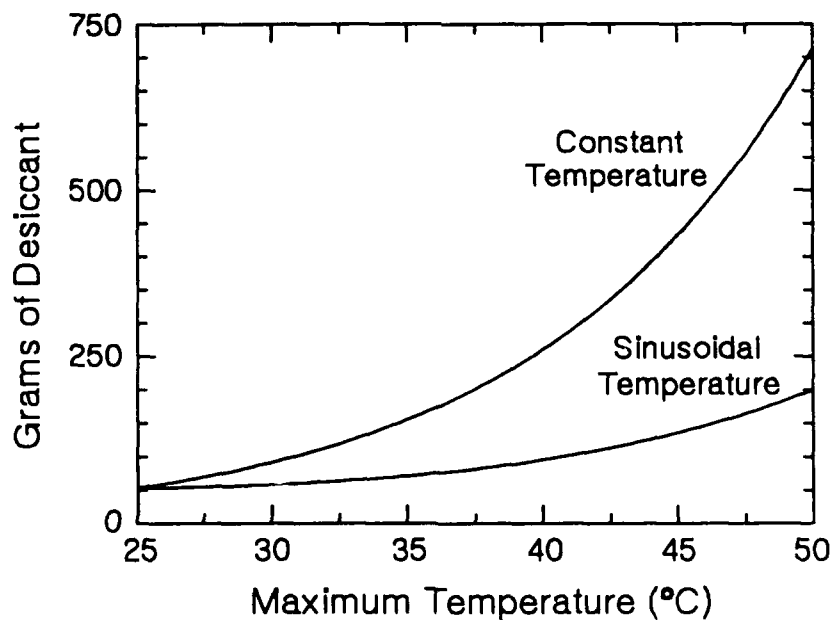
Fig. 13. Desiccant requirements of the polyethylene box at constant 50% relative humidity as a function of maximum storage temperature. Constant and sinusoidally varying temperatures are compared.

from Eq. 17. The total mass of water contained within a package at the end of its design life is the sum of the water initially sealed into the package and the water that leaks or permeates into the package during storage. The initial water content W_0 was computed in Eq. 18 and the latter contribution can be obtained by integrating Eq. 30. If it is assumed that the external water vapor partial pressure is always much greater than that in the interior of the package then

$$W = W_0 + \int_0^t C_T P_E \, dt' = W_0 + \frac{\int_0^t C_T P_E \, dt'}{\int_0^t dt'} \int_0^t dt' = W_0 + \langle C_T P_E \rangle t \qquad (37)$$

Typically, it is relatively simple to compute the integral average $\langle C_T P_E \rangle$ given arbitrary variations in the storage temperature and humidity. In order to use the equations based on isothermal and isobaric storage conditions, however, we require the individual averages $\langle C_T \rangle$ and $\langle P_E \rangle$ and, in general, the product of the integral averages $\langle C_T \rangle$ and $\langle P_E \rangle$ does not equal $\langle C_T P_E \rangle$. To overcome this difficulty in the present model, we will take P_E to correspond to the initial relative humidity at the mean storage temperature and set $\langle C_T \rangle = \langle C_T P_E \rangle / P_E$. The results for the polyethylene box subjected to a sinus-oidally varying environment that are obtained from this approximate method are shown by the symbols in Fig. 12. The agreement with the solution to Eq. 31 is excellent. The deviations in the constant pressure case at high temperature amplitudes result from the fact that the pressure is not truly constant, rather, at low temperatures the relative humidity is limited to 100%. In general, however, the approximate approach provides a good way to allow for a variable storage environment.

3. <u>Variable storage humidity</u>: the case of constant temperature, variable humidity storage can be treated approximately, once again, as described above. The technique, however, is much simpler here. At constant temperature, the total conductance of the package's seals is constant and we can replace $\langle C_T P_E \rangle$ in Eq. 37 by $C_T \langle P_E \rangle$. In other words, we can simply replace P_E in the isothermal equations with its integral average over the storage humidity profile.

EXAMPLE: FMU-139A/B CONVENTIONAL FUZE

As demonstrated above, a large number of factors must be considered when developing models for moisture control in a sealed package. In addition, the computations involved in the model are fairly complex and make extensive use of numerical methods. In order to facilitate the use of this model as a design tool, I have developed a computer program entitled MCONTROL which implements the moisture control model. The program has facilities for cre-ating package design models, computing desiccant requirements and evaluating interdependences among the various design and storage parameters. A complete outline of the structure, function and use of MCONTROL is given in Appendix C. Here, the use of MCONTROL will be illustrated by applying it to moisture control in a typical electronics package.

The polyethylene box example that was used above was chosen to accentuate the role of permeation in supplying water to the interior of a package. A more typical example of the problems encountered in electronic packaging is provided by considering moisture control in the FMU-139A/B conventional fuze. The FMU-139A/B fuze, manufactured by Motorola, currently has a six month service life. It is felt that moisture related degradation is the main factor limiting the service life and that by controlling the internal moisture content of the fuze, the service life could be extended. The FMU-139A/B contains a large quantity of organic material in the form of printed circuit boards, encapsulants and plastic mechanical components. It is also employs a number of elastomeric seals, some that are o-rings and some that are more readily modeled as planar barriers. This design permits all of the functions of the moisture control model to be exercised.

The package design and base-line storage parameters for the FMU-139A/B fuze are listed in Table 1. Table 1 was generated by using MCONTROL to create a model of the fuze and then employing the "Print Results" function of the program to list the model on a printer. The dimensions and masses of the seals and organic materials are estimates based on a dummy fuze and design drawings. Not all of the internal organic materials were considered. For example, Kapton flex cables and some insulating films were neglected as being insignificant compared to the total organic content of the package and the uncertainties inherent in the mass estimates.

For this example, the base-line design goal is to maintain the fuze's internal dew point below -20°C for a period of two years when the unprotected fuze is stored at room temperature and 50 %RH. The amount of Type 4A desiccant that must be incorporated into the package in order to achieve this goal, about 20 grams, is listed in Table 1. The predicted internal water vapor partial pressure and dew point increase with storage time, based on this quantity of desiccant, are plotted in Fig. 14. The amount of desiccant needed to
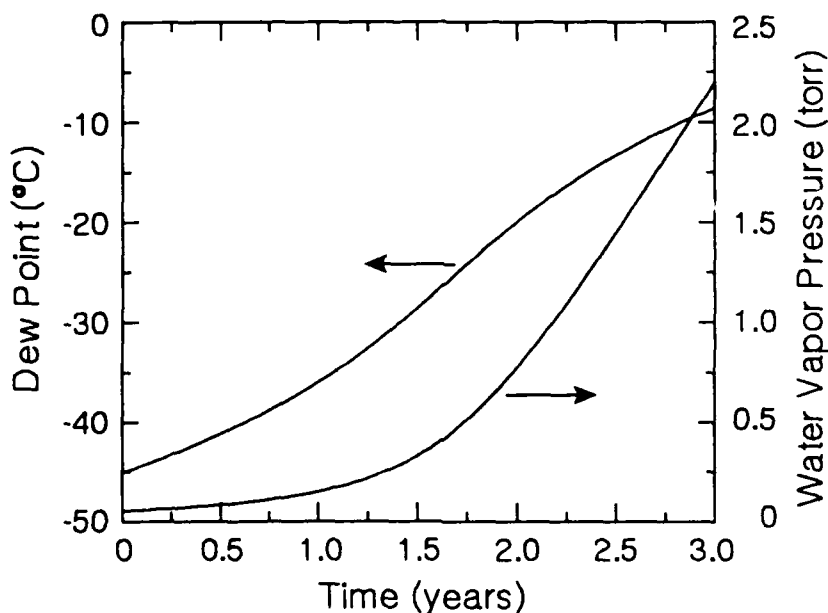
Fig. 14. Water vapor partial pressure and dew point inside the FMU-139A/B fuze as a function of storage time. The dew point will reach -20°C after 2 years.

Table 1. Output of the Print Results function of the MCONTROL program for the FMU-139A/B fuze.

```
                    FMU-139A/B Conventional Fuze


                         Storage Parameters

        Storage temperature = 23 C
        Storage relative humidity = 50%
        Design lifetime = 2 years
        Maximum internal dew point = -20 C
        Lower use temperature = -48 C
        Upper use temperature = 74 C



                         Package Parameters

        Free volume in package = 100 cc
        Free surface area in package = 1500 sq cm
        Temperature when the package was sealed = 23 C
        Humidity when the package was sealed = 50%
        Initial water content of package = 2.74277 grams
        Initial internal pressure = 0.0533544 torr



                     Absorbing Material Parameters

        Glass/Epoxy circuit board
            Mass = 75 grams
            Saturation uptake = 1.5 grams water/100 grams
            Equilibration humidity = 50%
            Initial absorbed water = 0.5625 grams

        Polyurethane encapsulant
            Mass = 75 grams
            Saturation uptake = 3 grams water/100 grams
            Equilibration humidity = 50%
            Initial absorbed water = 1.125 grams

        Poly phenylene oxide (insulators, detonator housing)
            Mass = 30 grams
            Saturation uptake = 0.3 grams water/100 grams
            Equilibration humidity = 50%
            Initial absorbed water = 0.045 grams

        Nylon/Glass (S&A rotor, lock block)
            Mass = 50 grams
            Saturation uptake = 4 grams water/100 grams
            Equilibration humidity = 50%
            Initial absorbed water = 1 grams

        Polycarbonate PWB cover
            Mass = 6 grams
            Saturation uptake = 0.3 grams water/100 grams
            Equilibration humidity = 50%
            Initial absorbed water = 0.009 grams

        Total mass of absorbing materials = 236 grams
        Composite saturation uptake = 2.32331 grams water/100 grams
        Water carried into package by organics = 2.7415 grams
```

Table 1. Continued.

```
                         Leakage Parameters

Helium leak rate = 1e-005 cc/sec
Equivalent conductance for water = 0.000156675 gram/year/torr

Miscellaneous water = 0 grams

Nitrile rubber bulkhead seal
     Permeability (25 C) = 5.7e-008 cc/cm-sec-torr
     Activation energy = 2.3 kcal/mole
     Permeability (23 C) = 5.5525e-008 cc/cm-sec-torr
     Length of o-ring = 22 cm
     Compression of o-ring = 25%
     Conductance for water = 0.0221751 g/year/torr

Nitrile rubber cap seal
     Permeability (25 C) = 5.7e-008 cc/cm-sec-torr
     Activation energy = 2.3 kcal/mole
     Permeability (23 C) = 5.5525e-008 cc/cm-sec-torr
     Length of o-ring = 7 cm
     Compression of o-ring = 25%
     Conductance for water = 0.00705572 g/year/torr

Nitrile rubber housing seal
     Permeability (25 C) = 5.7e-008 cc/cm-sec-torr
     Activation energy = 2.3 kcal/mole
     Permeability (23 C) = 5.5525e-008 cc/cm-sec-torr
     Length of o-ring = 22 cm
     Compression of o-ring = 25%
     Conductance for water = 0.0221751 g/year/torr

Nitrile rubber connector assembly seal
     Permeability (25 C) = 5.7e-008 cc/cm-sec-torr
     Activation energy = 2.3 kcal/mole
     Permeability (23 C) = 5.5525e-008 cc/cm-sec-torr
     Length of o-ring = 2.25 cm
     Compression of o-ring = 25%
     Conductance for water = 0.00226791 g/year/torr

Silicone gag rod seal
     Permeability (25 C) = 1.9e-007 cc/cm-sec-torr
     Activation energy = -2.2 kcal/mole
     Permeability (23 C) = 1.94825e-007 cc/cm-sec-torr
     Length of o-ring = 2 cm
     Compression of o-ring = 25%
     Conductance for water = 0.00707341 g/year/torr

Kraton plug seal
     Permeability (25 C) = 1e-008 cc/cm-sec-torr
     Activation energy = 4 kcal/mole
     Permeability (23 C) = 9.55429e-009 cc/cm-sec-torr
     Area of barrier = 3 sq cm
     Thickness of barrier = 0.3 cm
     Conductance for water = 0.0024217 g/year/torr

Nitrile rubber rotary switch seal
     Permeability (25 C) = 5.7e-008 cc/cm-sec-torr
     Activation energy = 2.3 kcal/mole
     Permeability (23 C) = 5.5525e-008 cc/cm-sec-torr
     Area of barrier = 0.68 sq cm
```

Table 1. Continued.

```
          Thickness of barrier = 0.76 cm
          Conductance for water = 0.00125923 g/year/torr

   Total water conductance = 0.0645849 g/year/torr



                   Molecular Sieve Parameters

   Type of sieve = 4A
   Sieve capacity used during assembly = 0 grams/100 grams
   Mass of sieves = 20.1974 grams
   Mass of sieves to maintain a -48 C dew point = 33.9595 grams
   Mass of sieves if equilibrated at 74 C = 41.208 grams
   Initial water in sieves = 0 grams


               Initial Non-equilibrated Water Distribution

   Mass of water in the volume = 0.00102739 grams
   Mass of water on surfaces = 0.0002457 grams
   Mass of water in materials = 2.7415 grams
   Mass of water in sieves = 0 grams
   Miscellaneous water = 0 grams
   Total water content = 2.74277 grams
   Pressure = 10.5331 torr,          Dew Point = 12.0279 C



               Initial Equilibrated Water Distribution

   Mass of water in the volume = 5.20417e-006 grams
   Mass of water on surfaces = 1.13972e-005 grams
   Mass of water in materials = 0.0138868 grams
   Mass of water in sieves = 2.72887 grams
   Total water content = 2.74277 grams
   Pressure = 0.0533544 torr,          Dew Point = -45.1002 C



                   Final Water Distribution

   Mass of water in the volume = 7.54825e-005 grams
   Mass of water on surfaces = 5.5993e-005 grams
   Mass of water in materials = 0.201418 grams
   Mass of water in sieves = 3.87177 grams
   Total water content = 4.07332 grams
   Pressure = 0.773865 torr,          Dew Point = -20 C
```

meet a -48°C (-55°F) dew point requirement, as well as the amount required to maintain a -20°C dew point while undergoing a temperature excursion to 74 °C (165°F), are also shown in the table. In order to account for the temperature jump, the requisite quantity of desiccant must, in this case, be doubled. Given the free volume available in the FMU-139A/B, it is clearly feasible to add sufficient desiccant to the package to control moisture at an innocuous level and extend the service life of the fuze.

Based on the amount of desiccant required to meet the maximum dew point specification, MCONTROL computes the initial water distributions, before and

after equilibration, and the predicted water distribution at the end of the design life, and these are shown in Table 1. It is interesting to note that over 2.7 grams of water are sealed into the package. Virtually all of this water is dissolved in the package's organic components. After the initial equilibration takes place, most of the water resides within the desiccant. This partitioning of the water reflects the much greater affinity for water possessed by the molecular sieves as compared to the organics. Comparing the initial and final distributions, we find that leakage and permeation contribute only another 1.3 grams to the package during exposure to service conditions. This indicates that most (68%) of the desiccant contained within the package will be used to dry the package out and that this amount must be included in the package even if it were to be hermetically sealed. Of course, the relative contributions of leakage and permeation increase with storage time. Figure 15 shows that the desiccant size needed to meet the -20°C dew point requirement varies linearly with design life.
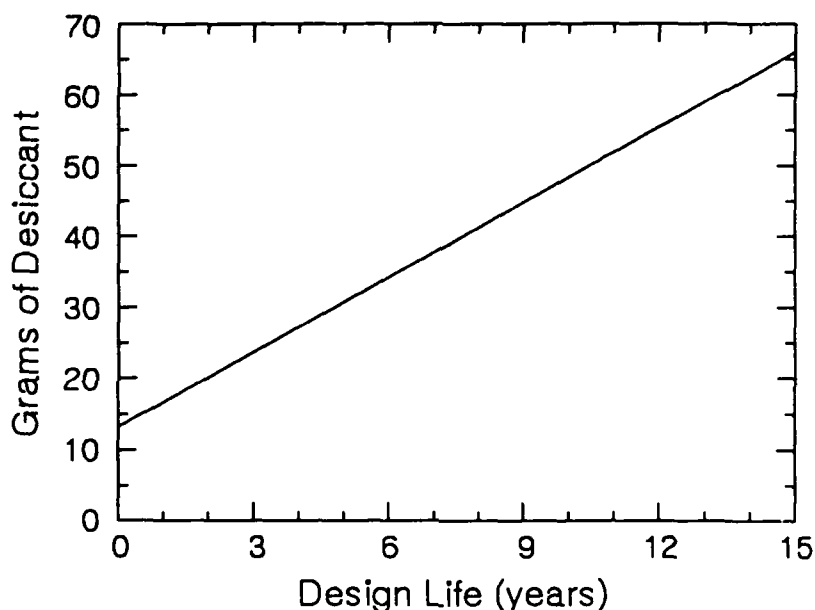
Fig. 15. Amount of desiccant required to control moisture in the FMU-139A/B fuze as a function of design lifetime.

The moisture distributions listed in the table show that essentially all of the water is contained within the molecular sieves and the organic materials. Consequently, estimates of the internal free volume and free surface area can be fairly crude. The major uncertainty in the model is the estimate of the amount of water carried into the package by the organic components. It has been assumed here that all of the materials were equilibrated at 50 %RH prior to sealing the package. If this is not the case, the amount of dissolved water will scale directly with the actual equilibration humidity. The effect on the line in Fig. 15 will be to raise or lower the intercept (in direct proportion to the equilibration humidity) while maintaining a constant slope.

MCONTROL itemizes the moisture contribution due to each of the organic components, as well as the moisture conductance of each of the seals. A comparison of the leakage conductance with the total conductance due to

permeation shows that leakage, as defined by the helium leak rate, will contribute negligibly to the total water load in the package. As a result, stringent helium leak rate requirements are not effective for controlling moisture. This is illustrated in Fig. 16 which shows the requisite desiccant size as a function of the package's helium leak rate. Leakage does not significantly effect the required desiccant size until the helium leak rate has surpassed 10^{-3} cm^3/sec. It is also clear, however, that a grossly leaking container cannot be tolerated.
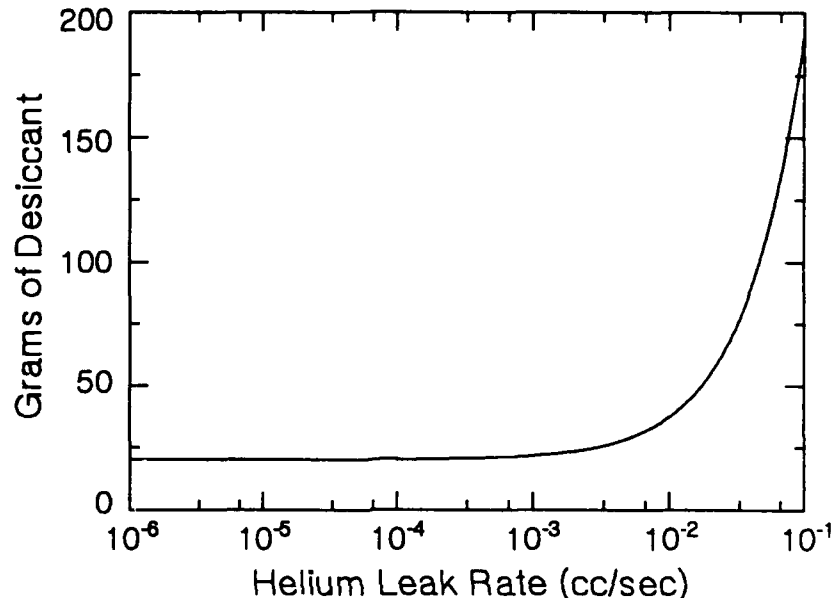
Fig. 16.   Effect of the helium leak rate on the computed desiccant requirements of the FMU-139A/B.

As expected, and shown in Table 1, the major routes of moisture ingress are through the main housing seal and the bulkhead seal. Both of these seals are fabricated from nitrile rubber. Nitrile rubber, as shown in Appendix D, is highly permeable to water. This suggests that replacing the nitrile rubber seal with one made of a less permeable material, such as EPR rubber, could decrease the permeated water contribution by about a factor of ten. In terms of the desiccant size vs. lifetime line in Fig. 15, lowering the seal permeability would decrease the slope of the line by the ratio of the permeabilities while keeping the intercept constant.

A major strength of the MCONTROL program lies in its ability to examine interdependences among the various storage and design parameters. A couple of these have already been mentioned, namely, the variation of the desiccant size needed to meet the specified moisture limit with design lifetime and helium leak rate. The desiccant size will also vary with the maximum dew point specification. This is shown in Fig. 17. The shape of this curve is fairly general in that, while it is relatively flat in the vicinity of the -20°C, it becomes increasingly more difficult to maintain the dew point as the specified limit is lowered further.

The storage environment also has a large impact on the calculated desiccant size. Figure 18 illustrates how the required desiccant size varies with isothermal storage temperature. If the external humidity remains constant at
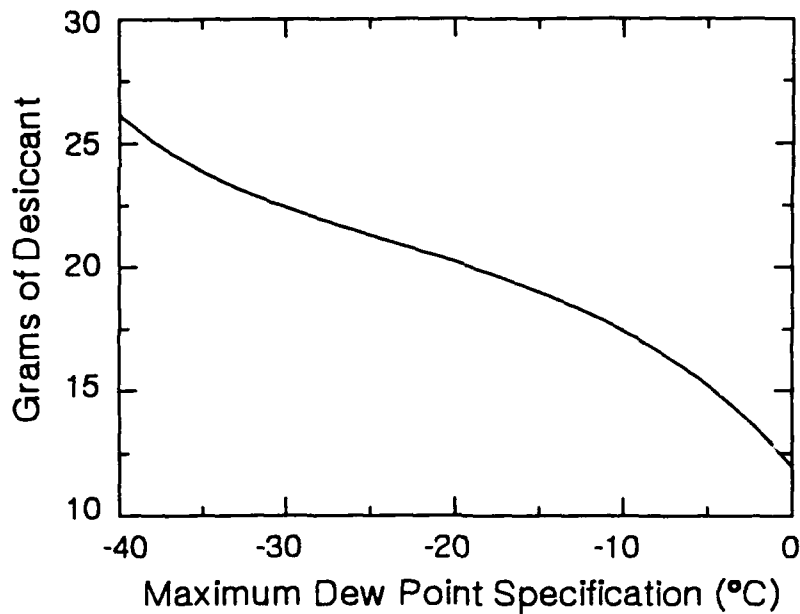
Fig. 17. Variation of the FMU-139A/B's desiccant requirement with its maximum dew point specification.
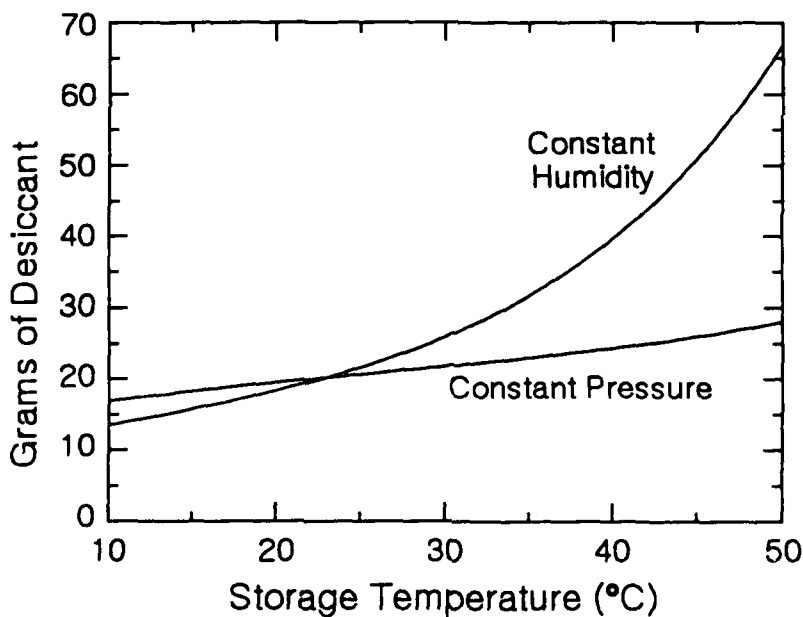
Fig. 18. Variation of the FMU-139A/B's desiccant requirement with isothermal storage temperature.

50%, the desiccant size increases rapidly with storage temperature. In the case of the FMU-139A/B fuze, storage at 40 °C requires about twice as much desiccant as would be needed for room temperature storage. If, on the other hand, the storage temperature varies sinusoidally, only a modest increase in the desiccant size is required as shown in Fig. 19. Variations in the storage
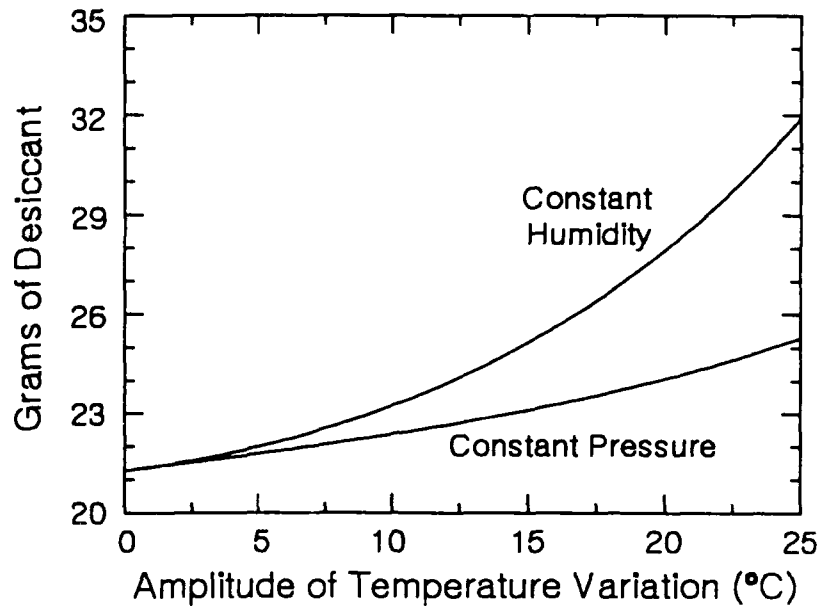
Fig. 19. Quantity of desiccant required for moisture control in an FMU-139A/B fuze subjected to a sinusoidally varying temperature.
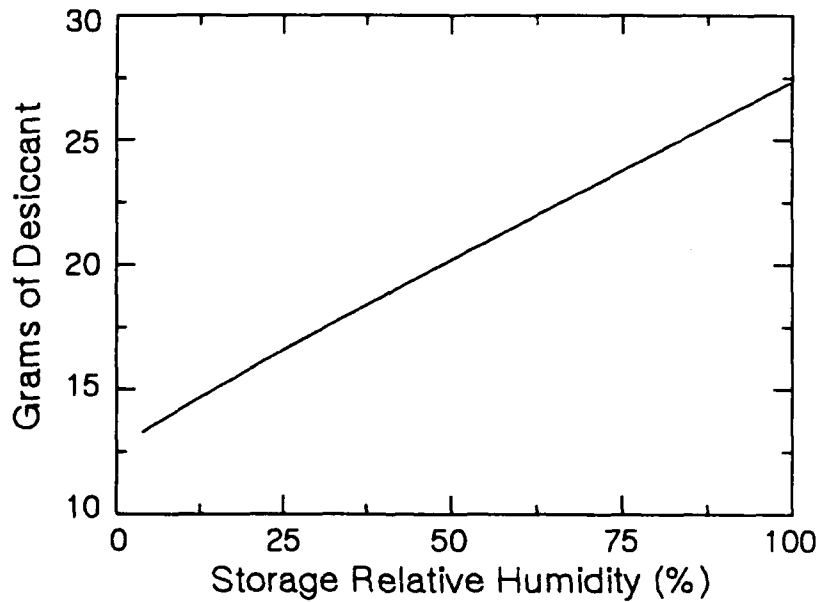
Fig. 20. Effect of isobaric storage humidity on the desiccant requirements of the FMU-139A/B fuze.

humidity generally have a smaller effect on desiccant size than those in temperature. As displayed in Fig. 20, desiccant size varies linearly with isobaric storage humidity, where, once again, the intercept is fixed by the water that is sealed into the package.

Besides the dependences that have just been treated, MCONTROL has facilities for examining many other interrelationships. One might be interested, for example, in knowing how the lifetime of a package will vary with the storage temperature if the desiccant size is held constant. The complete list of possible comparisons is given in Appendix C. Exploration of these facets of the moisture control problem, however, will be left, as they say, as an exercise for the reader.

LOCATING THE DESICCANT IN A PACKAGE

In the preceding model development, it has been assumed that internal moisture equilibrium is maintained at all times among the free volume, the free surfaces, the organic materials and the desiccant contained in a package. Implicit in this assumption is the requirement that water transport within a package must not be hindered. Oftentimes, especially when the interior of a package is filled with an encapsulant, this requirement will not be met. Consequently, in non-hermetic packages, localized areas of high moisture concentration can develop and persist in the steady state. In this section, I will develop expressions to gauge the extent of steady-state water concentration inhomogeneity in a package. I will also present some mechanical design guidelines that are intended to minimize these inhomogeneities and their effects.

Consider the idealized package sketched below in Fig. 21. The lid is sealed to the rest of the container with a single o-ring. Water leaks and permeates through the seal into a free volume V which is separated from the
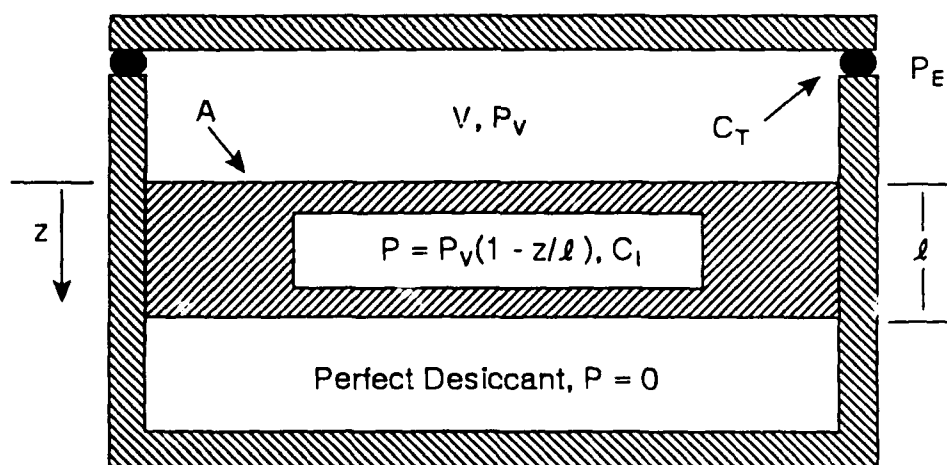
Fig. 21. Idealized view of an o-ring sealed package where the location of moisture ingress is separated from the desiccant by an encapsulant.

desiccant by a slab of encapsulant. The encapsulant has free surface area A and thickness ℓ. It will also be assumed that the desiccant is a perfect water getter, that is, the water vapor partial pressure at the surface of the desiccant is identically zero and sufficient desiccant is present to adsorb all of the water reaching it. At steady state, the rate at which water enters

the free volume of the package through the seal is equal to the rate that it diffuses out through the encapsulant. From Eq. 20,

$$C_T(P_E - P_V) = C_I P_V \qquad (38)$$

where C_T is the total conductance of the seal and C_I represents the conductance of the internal path that the moisture must traverse from the leak to the desiccant. For a planar barrier, C_I is given by Eq. 24. Rearranging yields

$$\frac{P_V}{P_E} = \frac{C_T}{C_T + C_I} = \frac{1}{1 + C_I/C_T} \qquad (39)$$

Equation 39 is plotted in Fig. 22. If the internal conductance is much smaller
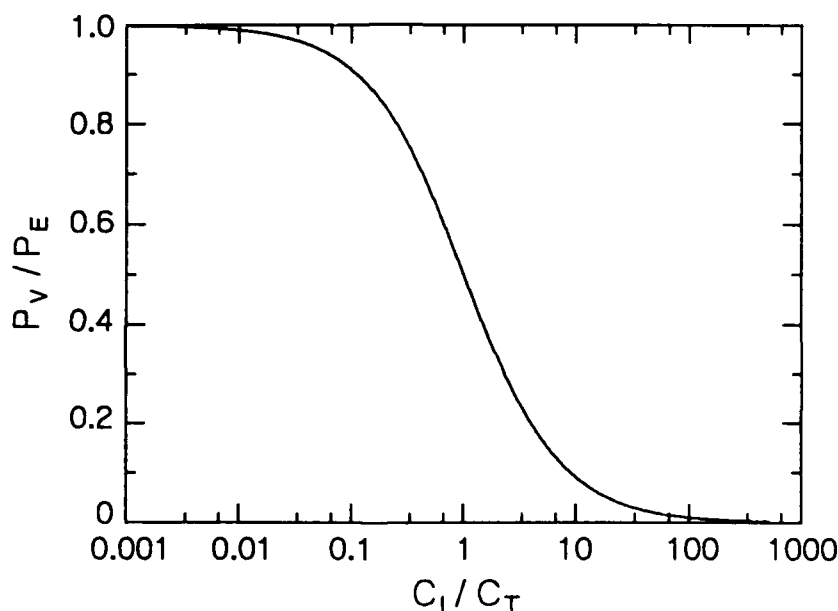
Fig. 22. Effect of a finite internal conductance on the steady-state pressure in the free volume of a leaking container.

than the leakage and permeation conductances, then the water vapor partial pressure in the free volume will approach that of the external storage environment and the desiccant will not be effective. If, on the other hand, the model assumptions are to be satisfied and the interior of the package is to be dried uniformly, C_I/C_T must be greater than about 100.

While it is clear that a material barrier will impede the internal transport of moisture in a package, it should be noted that air, in a sufficiently constrained geometry, will also prove an impediment. The permeability of water in stagnant air[25] is about 2.9×10^{-4} std cc/(cm·sec·torr) and the expressions developed earlier can be used to calculate the conductance. For example, the conductance of a normal drinking straw is found to be about 0.1 g/(yr·torr). If the interior of the FMU-139A/B fuze were to be connected

to a perfect desiccant through this straw, Eq. 39 would predict that the steady-state water vapor pressure in the fuze would correspond to about 40% of the ambient humidity. In this case, poor location of the desiccant relative to the points of leakage and permeation would render the desiccant ineffective at controlling the moisture level in the fuze.

In the encapsulation scenario that was outlined above, it was shown that large steady-state humidities can develop in the free volume of a package. At a first glance, this might appear to be acceptable since the electronics would seem to be protected by the encapsulation. This will not always be the case, however. If the water vapor pressure in the free volume differs from that in the vicinity of the desiccant, a steady-state concentration gradient will develop in the encapsulant. The nature of this gradient is governed by the diffusion equation and will be geometry dependent. In the case shown above, where the encapsulant is exposed to moisture over a plane surface, the effective partial pressure of water will decrease linearly through the depth of the encapsulant:

$$P = P_V(1 - z/\ell) \tag{40}$$

where z is the distance measured from the surface of the encapsulant. This would be the water vapor partial pressure found, for example, in the cells of a foam, in a crack or void, or at the interface with an electronic component having little adhesion to the encapsulant. While the environment within the encapsulant might be less severe than that in the free volume, it may still contain more moisture than would be desirable for high reliability operation.

The exposure of a plane surface of the encapsulant to moisture provides a worst case. The situation is improved considerably if the exposure occurs along a line, for example, at the interface with an o-ring seal, or at a point. These geometries are conveniently modeled in terms of hollow cylinders or hollow spheres and, for completeness, the permeation conductances and effective partial pressure profiles for these geometries are listed in Table 2. In the table, a and b represent, respectively, the inner and outer radii of the cylinder or sphere and r is the radial coordinate. L is the length of the cylinder. When computing the partial pressure profiles, it is also assumed that the partial pressure of water at the surface of the desiccant is identically zero.

Table 2. Permeation conductances and effective partial pressure profiles for three typical geometries.[20]

Geometry	Permeation Conductance	Partial Pressure Profile
Plane Sheet	QA/ℓ	$P_V(1 - z/\ell)$
Hollow Cylinder	$\dfrac{2\pi LQ}{\ln(b/a)}$	$P_V \dfrac{\ln(b/r)}{\ln(b/a)}$
Hollow Sphere	$\dfrac{4\pi abQ}{b - a}$	$P_V \dfrac{a(b - r)}{r(b - a)}$

In the cylindrical and spherical geometries, the effective partial pressure drops off more rapidly with distance than does that in the plane sheet. This is illustrated in Fig. 23 where, for the cylinder and sphere, b/a was taken to be 10. As b/a increases, the pressure decreases even more rapidly, whereas, as b/a → 1, the plane sheet limit is approached.
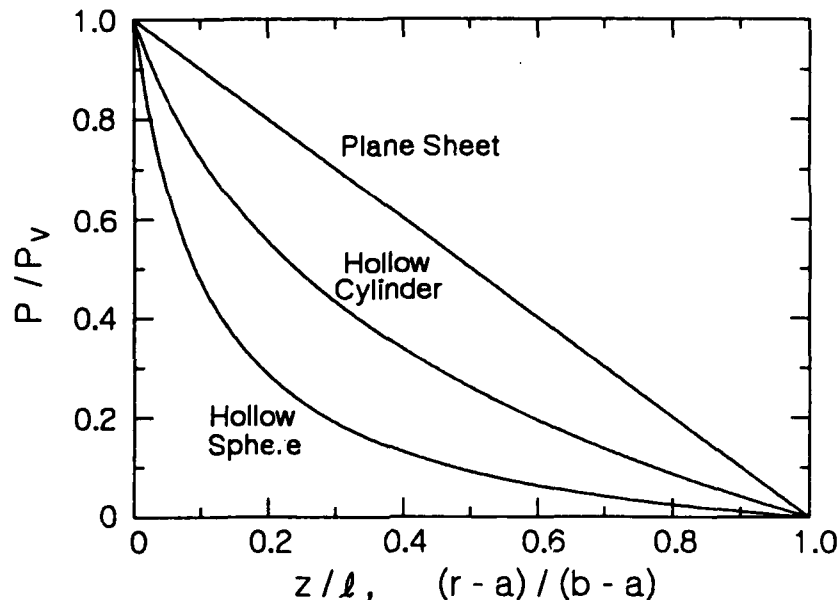
Fig. 23. Concentration profiles at steady state through the thickness of an encapsulant for three different geometries. For the cylinder and sphere, b/a - 10.

Traditionally, when designing desiccated packages, little thought has been given to where the desiccant should be physically located in the package. Rather, it would be placed wherever there happened to be enough room to accommodate it. I hope the foregoing discussion has pointed out some of the dangers attendant upon that approach and makes a case for considering desiccant location as an integral part of a package's mechanical design. This is particularly true in the case of encapsulated electronics. I have listed below, some guidelines to assist in choosing the proper desiccant placement:

1. Place the desiccant in close proximity to the components that are to be protected.

2. Place the desiccant between the components to be protected and the source of moisture (leak or organic seal) so that the desiccant will intercept the moisture before it reaches these components. If the locations of the desiccant and the encapsulant in Fig. 21 were swapped in accordance with this rule, no steady-state water concentration gradients would develop.

3. If room for extra desiccant is available, disperse it throughout the package. This has two beneficial effects. The moisture concentration in the package will remain more uniformly low and the time to reach internal equilibrium will be drastically shortened.

4. For encapsulated electronics, maintain good adhesion between the encapsulant and the package housing. This will minimize the surface area of encapsulant exposed to the external source of moisture which, in turn, will minimize the penetration depths of any concentration gradients that do develop.

While these steps are simply common sense, they must be considered and adhered to in the package design in order to ensure optimum desiccant performance.

SUMMARY

The general problem of moisture control in electronics packaging, both hermetic and nonhermetic, has been investigated. The deleterious effects of moisture on electronic assemblies have been outlined and some thought has been given to what constitutes an acceptable moisture level within an electronics package. Based on the evidence that is presented, I recommend that packages be designed to meet a -20 °C maximum dew point requirement. This represents a reasonable compromise between avoiding moisture-related failure and the difficulty and cost of complying with a stricter specification.

The basic strategy for controlling moisture is to incorporate desiccant into the package and the superiority of molecular sieves in this task was demonstrated. The desiccant acts by sequestering the vast majority of the water inside a package in a harmless location. The total quantity of water that must be accounted for in this fashion can be divided into two contributions, water that is sealed into the package at assembly time and water that leaks or permeates into the package during storage. Often, as exemplified by the FMU-139A/B fuze, the bulk of the total water is present in the package when it is sealed. Desiccant must be included in the package to adsorb this water even if the package is hermetically sealed.

In order to assist the package designer with the job of controlling moisture, a mathematical model describing the sources, sinks and partitioning of water within a package was developed. This model can be used to calculate the amount of desiccant required to meet the design objectives and to explore interrelationships among the design and storage parameters. In contrast to previous models, the actual Langmuir-like adsorption isotherm is used to describe the water absorption characteristics of molecular sieves. This permits a much more realistic depiction of the behavior of water within a package. In addition, the dependence upon temperature of each of the model parameters is explicitly treated in order to evaluate the impact of a variable storage environment on the requisite desiccant size.

A computer program, MCONTROL, was written for IBM PC compatible computers to implement the moisture control model. The structure, function and use of the program was outlined and its application was illustrated by considering moisture control in the FMU-139A/B conventional fuze. The results indicated that moisture within the fuze can be maintained at acceptable levels by incorporating desiccant into the design. This should allow the service life of the fuze to be extended significantly.

As a final caution, the effects of the physical placement of desiccant inside the package and long-term material aging and degradation are not easily modeled and have not been included in the model developed here. Instead, some guidelines were given that relate to the proper placement of desiccant in a package to maximize its effectiveness. The reader is also urged to take care

when selecting seal materials to consider their stabilities and resistances to the anticipated storage environment.

REFERENCES

1. R. W. Thomas, "Moisture, Myths and Microcircuits," IEEE Trans. Parts, Hybrids and Packaging, PHP-12, 167 (1976).

2. R. H. Delaney and J. N. Lahti, "Accelerated Life Testing of Flexible Printed Circuits, Part II," 14th Annual Proceedings, IEEE Reliability Physics Symposium, p. 114 (1976).

3. The saturation pressure of water vapor as a function of temperature was computed using the formulas of J. A. Goff and S. Gratch, Trans. Amer. Soc. Heat. and Vent. Eng. 52, 95 (1946) as presented in "Selecting Humidity Sensors for Industrial Processes Handbook," General Eastern Instruments Corporation, March 1982.

4. P. W. Atkins, Physical Chemistry, W. H. Freeman and Company, San Francisco, 1978.

5. K. E. Mead, "The Need for Desiccant in Containers Exposed to Atmospheric Conditions for Long Periods of Time," Sandia Report SAND81-1898, November 1981.

6. R. P. Merrett, S. P. Sim and J. P. Bryant, "A Simple Method of Using the Die of an Integrated Circuit to Measure the Relative Humidity Inside Its Encapsulation," 18th Annual Proceedings, IEEE Reliability Physics Symposium, p. 17 (1980).

7. J. G. Davy, "How to Calculate the True Permissible Leak Rate and How to Raise it by Four Orders of Magnitude," IEEE Trans. Components, Hybrids, and Manufact. Tech. CHMT-8, 359 (1985).

8. J. G. Davy, "Thermodynamic and Kinetic Considerations of Moisture Sorption Phenomena," in Moisture Measurement Technology for Hermetic Semiconductor Devices, NBS Special Pub. 400-72, p. 184 (1980).

9. D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, "Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A," J. Am. Chem. Soc. 78, 5963 (1956).

10. T. B. Reed and D. W. Breck, "Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A," J. Am. Chem. Soc. 78, 5972 (1956).

11. "Davison Molecular Sieves," W. R. Grace & Co.

12. R. H. Dungan and J. A. Gilbert, "Epoxy-Bonded Molecular-Sieve Desiccants," Sandia Report SC-DR-69-25, February 1969.

13. C. K. Hersh, Molecular Sieves, Reinhold Publishing Corp., New York, 1961.

14. J. A. Barrie, "Water in Polymers", in <u>Diffusion in Polymers</u>, J. Crank and G. S. Park, eds., Academic Press, New York, 1968, p. 259.

15. B. Morris, "Heats of Sorption in the Crystalline Linde-A Zeolite-Water Vapor System," J. Colloid and Interface Sci. <u>28</u>, 149 (1968).

16. J. F. O'Hanlon, <u>A User's Guide to Vacuum Technology</u>, John Wiley & Sons, New York, 1980.

17. J. Crank and G. S. Park, "Methods of Measurement", in <u>Diffusion in Polymers</u>, J. Crank and G. S. Park, eds., Academic Press, New York, 1968, p. 1.

18. J. G. Davy, "Calculations for Leak Rates of Hermetic Packages," IEEE Trans. Parts, Hybrids and Packaging, <u>PHP-11</u>, 177 (1975).

19. K. T. Gillen, "A Better Method for Estimating Long-Term Ingress of Water into Weapons Based on Argon Gas Concentration," Sandia Report SAND87-0809, May 1987.

20. J. Crank, <u>Mathematics of Diffusion, 2nd ed.</u>, Oxford University Press, London, 1975.

21. I. S Gradshteyn and I. M. Ryzhik, <u>Table of Integrals, Series and Products</u>, Academic Press, New York, 1965.

22. H. Yamaguchi, "Water Vapor Absorption and Permeability of Epoxy Resins," Proc. 15th IEEE Elect./Electron. Insul. Conf., 159 (1981).

23. M. R. Keenan, "Moisture Permeation into Nuclear Reactor Pressure Transmitters," Sandia Report SAND83-2165, March 1984.

24. All numerical results presented here were computed using routines given in W. H. Press, et. al., <u>Numerical Recipes in C: The Art of Scientific Computing</u>, Cambridge University Press, 1988.

25. C. J. Hilado and R. H. Harding, "Some Relationships between Water Vapor Permeability and Chemical/Physical Structure in Rigid Urethane Foams," J. Appl. Poly. Sci. <u>7</u>, 1775 (1963).

26. Permeation coefficients were calculated from data presented in R. D. Helander and W. B. Tolley, "Water Vapor Transmission Rate (WVTR) of Elastomeric Materials," Proceedings 29th National SAMPE Symposium, 1373 (1984).

27. P. G. Kelleher and D. J. Boyle, "Gaging Moisture Vapor Permeability of Plastic Molding Compounds," Modern Plastics, November, 1979, p. 82.

28. H. Yasuda and V. Stannett, "Permeability Coefficients," in <u>Polymer Handbook, 2nd ed.</u>, J. Brandrup and E. H. Immergut, Eds., John Wiley & Sons, New York, 1975, p. III-229.

29. S. T. Hwang, C. K. Choi and K. Kammermeyer, "Gaseous Transfer Coefficients in Membranes," Separation Science <u>9</u>, 461 (1975).

30. P. E. Cassidy and T. M. Aminabhavi, "Water Permeation Through Elastomers and Plastics," Rubber Chem. and Tech. 56, 595 (1983).

31. E. Sacher and J. R. Susko, "Water Permeation of Polymer Films. IV. Teflon FEP," J. Appl. Poly. Sci. 27, 3893 (1982).

32. E. Sacher and J. R. Susko, "Water Permeation of Polymer Films. I. Poly-imide," J. Appl. Poly. Sci. 23, 2355 (1979).

APPENDIX A: SYMBOLS, CONSTANTS AND CONVERSIONS

The list below defines the major symbols, constants and conversions that were employed in this report.

a, b   Inner and outer radii, respectively, for a hollow cylinder or sphere.

A   Free surface area in the interior of a package in cm^2; surface area of a plane sheet of material.

b, c, n   Constants describing the Langmuir-like adsorption isotherm of molecular sieves.

C   Conductance in cc/sec relating the flux of water into a package to the water vapor partial pressure differential across the package's seals.

C_I Internal conductance of a sealed package.

C_L Conductance of a package resulting from leakage.

C_O Conductance of an o-ring seal resulting from permeation.

C_P Permeation conductance of miscellaneous organic barriers.

C_T Total conductance of a package, $C_T = C_L + C_O + C_P$.

C0, C1, C2   Concentrations of water in g/cm^3 serving as boundary and initial conditions in the solution of the transient permeation problem.

D   Diffusion coefficient in cm^2/sec.

E   Activation energy for permeation through an organic material in kcal/mole.

f(T)   Clausius-Clapeyron equation describing the temperature dependence of the equilibrium water adsorption in molecular sieve desiccant.

F   Flux of water vapor through the seals of a package. Typical units are std cc/sec or gram/year.

G(S)   Empirical factor to correct the flux through a compressed o-ring as calculated by assuming a rectangular cross section.

ΔH Heat of sorption for water adsorbed in molecular sieve desiccant = 14 kcal/mole.

K_H Henry's law constant for the solubility of water in organic materials.

K_H' Henry's law constant approximating the adsorption of molecular sieves.

K_S Constant describing the surface adsorption of water = 3×10^{-7} g/cm^2.

ℓ	Thickness of a plane sheet of material.
L	Circumference of an o-ring seal in cm; length of a cylinder.
M_{He}	Atomic weight of helium = 4 g/mole.
M_o	Molecular weight of water = 18 g/mole.
M_D	Mass of molecular sieve desiccant in a package in grams.
M_D'	Mass of molecular sieves computed using the Henry's law approximation.
M_M	Mass of Henry's law absorbing materials (organics) in grams.
P	Partial pressure of water vapor inside a package in torr.
P_E	Water vapor partial pressure in the external storage environment.
P_0	Initial water vapor partial pressure in a package after the internal components have reached equilibrium.
P_S	Water vapor partial pressure inside the a package at the time it is sealed and before the internal components begin to equilibrate.
$P_S(T)$	Saturation water vapor pressure at the temperature T. From Ref. 3,

$$\log(P_S(T)) = -7.90298(373.16/T - 1) + 5.02808\log(373.16/T)$$
$$-1.3816\times10^{-7}(10^{11.344(1 - T/373.16)} - 1)$$
$$+8.1328\times10^{-3}(10^{-3.49149(373.16/T-1)} - 1) + \log(1013.246)$$

when water vapor is in equilibrium with liquid water and

$$\log(P_S(T)) = -9.09718(273.16/T - 1) - 3.56654\log(273.16/T)$$
$$+0.876793(1 - T/273.16) + \log(6.1071)$$

when it is in equilibrium with ice. T is the absolute temperature, log is the common logarithm and $P_S(T)$ is given in mbar. The pressure in torr is obtained by multiplying this result by 0.750065.

P_T	Total pressure including all gases and vapors in the atmosphere.
P_V	Water vapor partial pressure in the free volume of a package.
ppmv	Water vapor concentration in parts per million by volume.
ρ	Mass density of water vapor in the atmosphere in μg/cm^3.
Q	Permeability coefficient in std cc/(cm$\cdot$sec$\cdot$torr).
Q_0	Pre-exponential factor for the permeability coefficient.
r	Radial coordinate in a cylinder or sphere.

R	Gas constant $= 0.08206$ liter·atm/(mole·K)
	$= 1.9872$ cal/(mole·K)
	$= 62363$ cm^3·torr/(mole·K)

%RH   Relative humidity expressed as a per cent.

RH   Relative humidity when used as a fraction in some calculations.

RH_I Internal relative humidity of a package.

RH_E Relative humidity at which organic materials were equilibrated prior to being sealed into a package.

RH_S Relative humidity in the external environment at the time a package was sealed.

S   Compressive strain applied to an o-ring to make a seal.

S(P,T)   Equilibrium sorption of molecular sieve desiccant in g/g at temperature T and water vapor partial pressure P.

t   Time in seconds or years as appropriate.

T   Absolute temperature in K, isothermal storage temperature.

T_d Dew point temperature.

T_f Frost point temperature.

T_S Environmental temperature at the time a package is sealed.

T_0 Average storage temperature.

ΔT Amplitude of a sinusoidal storage temperature variation.

U_D Capacity of molecular sieve desiccant in g/g that was used up during the assembly of a package.

V   Internal free volume of a package in cm^3.

W   Total mass of water inside a package in grams.

W_A Mass of water contained in the internal atmosphere of a package.

W_D Mass of water adsorbed by molecular sieve desiccant.

W_M Mass of water dissolved in organic materials.

W_0 Mass of water inside a package immediately after it is sealed.

W_S Mass of water adsorbed to free surfaces in a package.

W_t Total mass of water that has leaked or permeated into a package in a time t after sealing.

W_{TP} Mass of water entering a package through transient permeation.

W_X Mass of miscellaneous water that was sealed into a package.

z   Thickness coordinate for a plane sheet.

Permeability Conversions

1 std cc/(cm·sec·cm Hg) = 0.1 std cc/(cm·sec·torr)

1 barrer = 10^{-11} std cc/(cm·sec·torr)

1 perm·in = 2.41×10^{-6} std cc/(cm·sec·torr)

Water Permeation and Leakage Conversions

1 std cc = 8.03×10^{-4} grams

1 std cc (H_2O)/sec = 8.03×10^{-4} grams/sec = 2.53×10^4 grams/year

1 std cc/(cm·sec·torr) = 2.53×10^4 grams/(cm·year·torr)

Miscellaneous Conversions

$T(K) = T(°C) + 273.16$

1 atm = 760 torr = 1013.25 mbar

1 year = 31,536,000 sec

Volume of 1 mole of ideal gas at 0 °C and 1 atm = 22414 std cc

APPENDIX B: PERMEATION THROUGH COMPRESSED O-RINGS

When computing the rate that gases or vapors permeate through an o-ring seal, the cross section of the compressed o-ring is generally assumed to be rectangular in shape. This allows the permeation flux to be estimated from Eq. 22

$$F = QA(P_E - P)/\ell \qquad (B1)$$

where Q is the permeability of the seal material, A is the exposed surface area ℓ is the seal thickness and $P_E - P$ is the partial pressure difference across the seal. A problem arises, however, in selecting appropriate values for A and ℓ. As Gillen has noted,[19] different choices of A and ℓ have, in the past, given rise to fluxes that differ among themselves by a factor of 3. To rectify this situation, he proposed an intuitively appealing expression for the flux

$$F = \left(\frac{4}{\pi}\right)QL(P_E - P)(1 - S)^2 G(S) \qquad (B2)$$

where L is the circumferential length of the o-ring, S is the compressive strain applied to the o-ring to make the seal and G(S) is an empirical correction factor that can be found in Parker's o-ring literature. This equation is obtained by equating the assumed rectangular seal cross section with the cross-sectional area of the uncompressed o-ring. In this appendix, I will evaluate this approximation by using the finite element method to compute the permeation flux through actual compressed o-ring cross-sectional geometries. In addition, I will investigate the effects of equatorial sealing, for example, to the sides of an o-ring groove, and will briefly treat transient permeation which has some bearing on the interpretation of helium leak rate data.

The finite element models developed here assume that the circumference of an o-ring is large relative to its cross-sectional diameter. The actual cross-sectional geometries are based on three photographs provided by K. T. Gillen that show the cross sections of radially unconstrained, compressed o-rings. The idealized compressed o-ring cross-sectional geometry is shown in Fig. B1 along with the required mensuration formulas. The cross-sectional areas computed from these

$$r = \frac{(w - \ell)^2 + 4h^2}{4(w - \ell)}$$

$$\sin(\theta) = h/r$$

$$A(\text{cross-sectional area}) = 2h\ell + 2\theta r^2 - 2h(r^2 - h^2)^{1/2}$$

$$R(\text{unstrained o-ring radius}) = (A/\pi)^{1/2}$$

$$S(\text{fractional strain}) = 1 - h/R$$

Fig. B1. Cross-sectional geometry and mensuration formulas for a compressed o-ring.

expressions agreed to within 2% with planimeter measurements made on the photographs. The uncompressed o-ring radii and compressive strains were then back-calculated. The compressions found, 13%, 25% and 40%, encompass the normal range employed in o-ring applications. Finite element meshes for the three o-rings are shown in Fig. B2, and Fig. B3 illustrates the three boundary

13% Compression

25% Compression

40% Compression
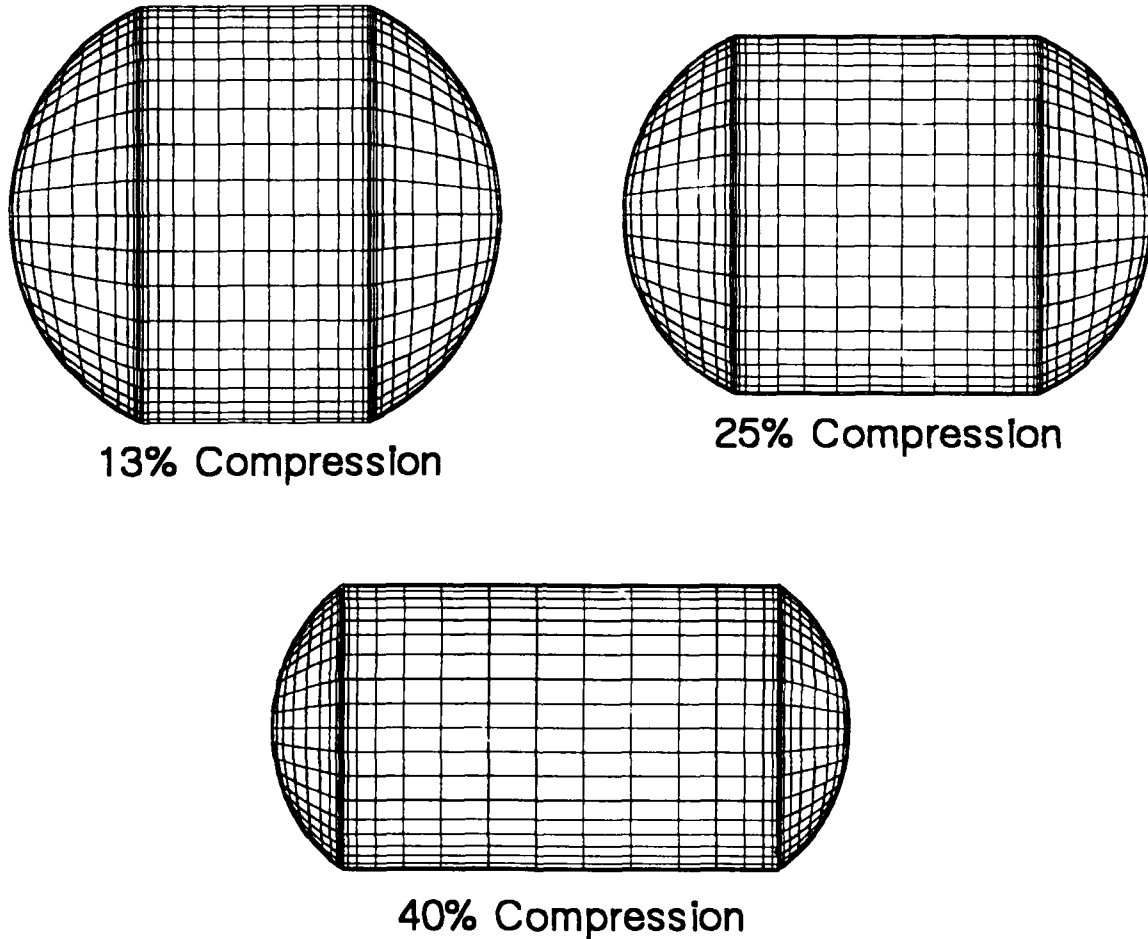
Fig. B2. Finite element meshes employed to compute the permeation flux through a compressed o-ring.

conditions that were considered. The effect of equatorial sealing was simulated by assuming that there is no flux across the sealed surface. This represents the best case situation in the sense that it should be most effective in lowering the permeation flux.

The factor G(S) can be estimated from the finite element results, being ratio of the true flux through the o-ring to the flux computed using the rectangular cross section approximation. Qualitatively, in the case of no equatorial sealing, G(S) should be greater than unity and approach 1 as the compressive stain increases. The rectangle approximation assumes that $<1/\ell>$ can be replaced by $1/<\ell>$ where $<>$ represents an average. In fact, for the curved surfaces, the shorter distances are weighted more heavily, thus, $<1/\ell> \geq 1/<\ell>$. This is borne out by the finite element calculations where G(S) was found to be 1.15, 1.09 and 1.01 at strains of 13, 25 and 40%, respec-

No Equatorial Seal

Pressure = 0   Pressure = P

Single Equatorial Seal

Double Equatorial Seal
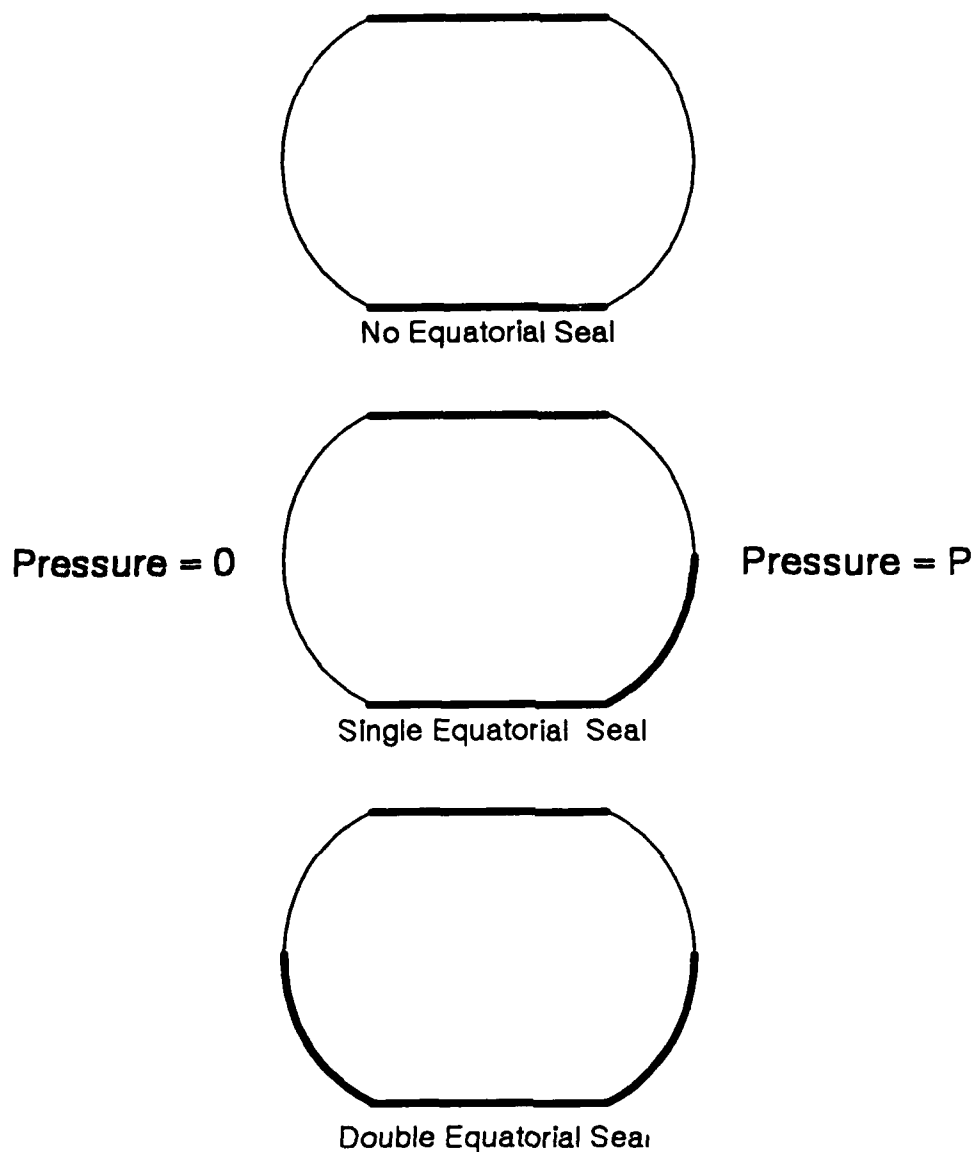
Fig. B3.   Boundary conditions employed in the finite element computation of permeation through an o-ring.   A heavy border indicates a no flux boundary, and the light border, a constant pressure boundary.

tively.   As shown by the top contour plot in Fig. B4, diffusion is primarily planar.

Poisson's ratio for elastomers is ≈0.5.   This means that as the o-ring is compressed, it expands in the radial direction while maintaining a constant volume.   As a result, an equatorial seal may form against the outside circumference of an o-ring groove.   Considering tolerances in the o-ring cross-sectional radii, groove machining and compression, it is also quite possible to form seals against both inner and outer circumferences of the groove.   If diffusion were to remain planar in these situations, the permeation flux would

No Equatorial Seal

Pressure = 0   Single Equatorial Seal   Pressure = P

Double Equatorial Seal
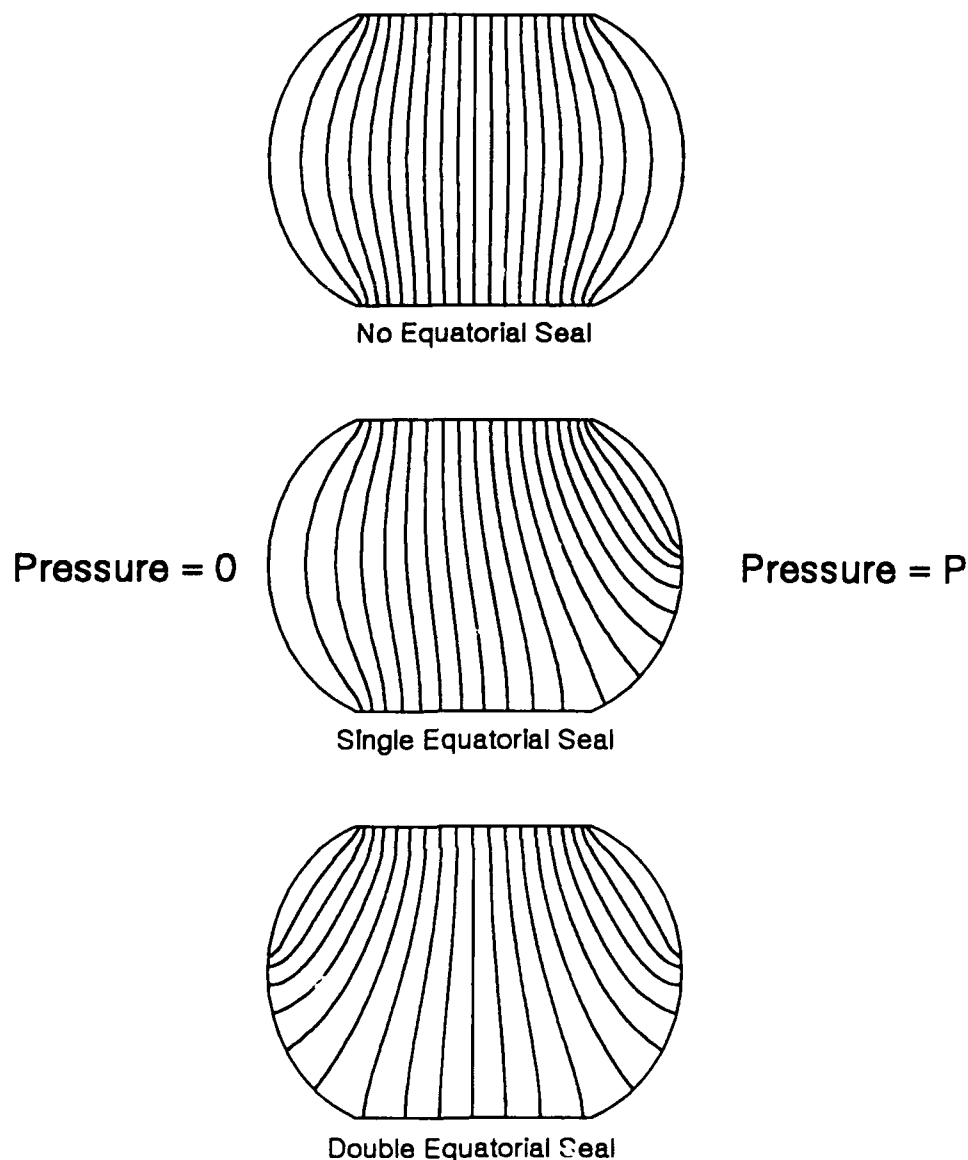
Fig. B4. Steady-state moisture distribution through the
cross section of a compressed o-ring. The contours represent
lines of constant concentration and are monotonically decreas-
ing from right to left in 5% steps.

be expected to decrease by a factor of 2 or more. Unfortunately, this is not
the case as shown by the middle and bottom contour plots in Fig. B4. The
total permeation through the o-ring is the product of the exposed area with
the concentration gradient at the surface. When part of the boundary is made
impermeable, the diffusing gas or vapor will spread out to fill the entire
volume of the rubber. In effect, smaller exposed surface areas are compensat-
ed, in part, by higher concentration gradients at the boundary. The net
result is that equatorial seals are only partially effective at lowering the
permeation flux. The computed values of G(S) and the degree of improvement in

-51-

the permeation flux caused by equatorial sealing are listed in the table below
and plotted in Fig. B5.

S	No Seal G	1 Equatorial Seal G_1	G_1/G	2 Equatorial Seals $\bar{G}_2$	$\bar{G}_2/G$
0.13	1.15	0.88	0.77	0.75	0.65
0.25	1.09	0.90	0.83	0.79	0.72
0.40	1.01	0.91	0.90	0.83	0.82

Equatorial sealing has the greatest effect at the smallest compressions.
Lower compressions, however, are much less likely to form equatorial seals.

Curves for G(S) taken from Parker's O-ring catalog are also reproduced in
Fig. B5. These curves are empirical in nature and depend on whether or not
the o-ring is lubricated. In the case of the dry o-ring, the values of G are
somewhat greater than the values computed here, especially at small compres-
sions. This may be related to seal imperfections that allow leakage past the
seal. One effect of lubricating the o-ring will be to help plug these leaks
and bring G closer to unity. The reason that the lubricated o-rings exhibit
values of $G \leq 1$ is not clear. This may indicate that lubricated o-rings more
easily form equatorial seals, that the cross-sectional geometry is changed, or
may be related to the barrier properties of the grease itself. In the last
case, the effect will be enhanced by squeeze out at the o-ring/sealing surface
junction which is the region of highest flux.
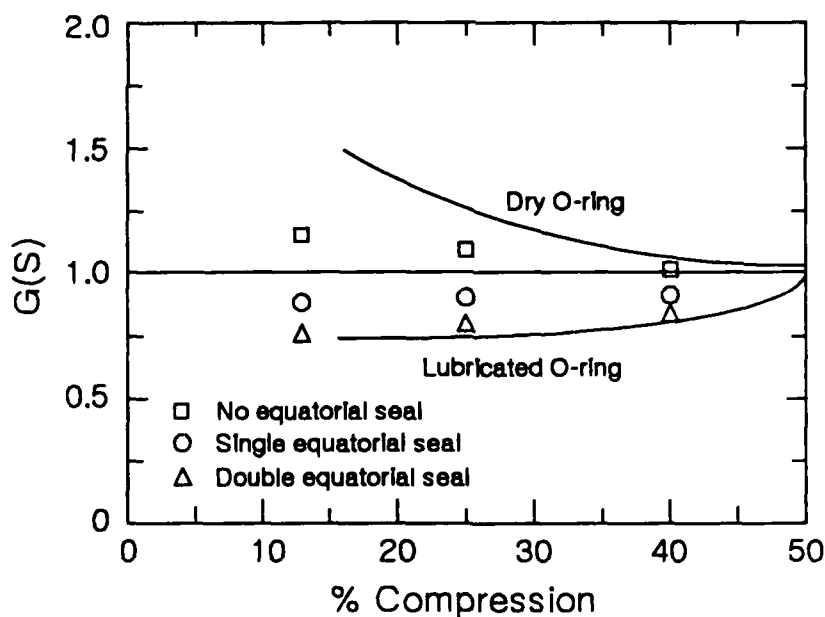
Fig. B5. Comparison of the computed G(S) correction
factor (symbols) with those provided in the Parker Co.
o-ring literature.

The generality of the G(S) curves supplied by Parker is unknown. Consid-
ering the variability in forming the seal (i.e. equatorial vs. no equatorial
sealing), the large uncertainties that typically attend permeability values,
and the general proximity of G(S) to unity, I feel that a reasonable approach

to estimating steady-state permeation fluxes is to simply set G(S) equal to 1. This is the approximation that was used in Eq. 25 of this report.

In the absence of material aging effects, the steady-state flux of gas or vapor through an o-ring seal is sufficient for lifetime ingress estimates. Transient permeation, on the other hand, is important for interpreting the results of leak tests that may be performed in a matter of hours after final assembly of a package. The rate at which the flux through a plane sheet comes to equilibrium is given by[20]

$$\frac{F(t)}{F(\infty)} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-Dn^2\pi^2 t/\ell^2} \tag{B3}$$

where D is the diffusion coefficient. The results of this equation are compared with finite element computations for the 25% compressed o-ring in Fig. B6. As expected, in the case of no equatorial seal, the actual flux reaches equilibrium more quickly than the rectangle approximation would predict. The equilibration time increases if equatorial seals are present which is related to the fact that the diffusant must permeate the entire volume of the o-ring at equilibrium. Clearly, if o-ring sealed systems are leak tested at times that correspond to the steep portion of the permeation curve and equatorial seals may or may not be present, large variations in the measured leak rate could be observed for equally good seals.
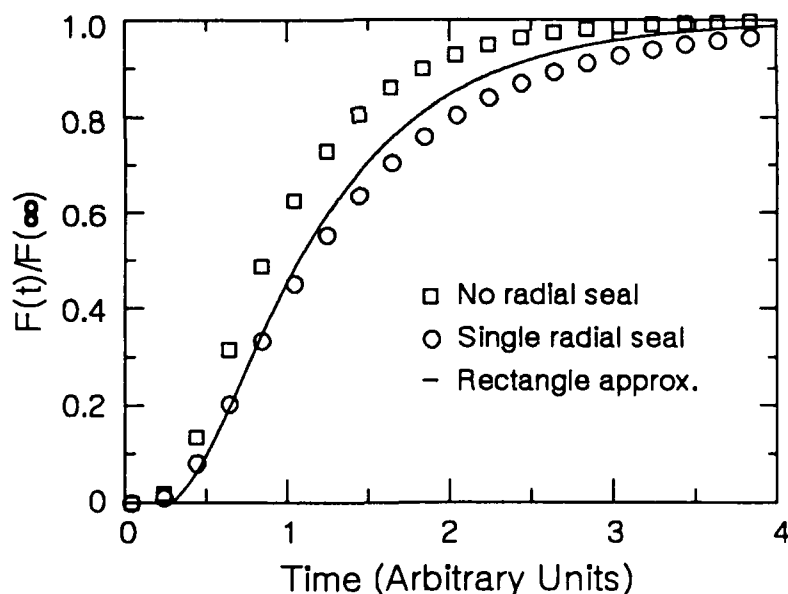
Fig. B6. Transient permeation through a compressed o-ring.

APPENDIX C: MCONTROL PROGRAM

A computer program entitled MCONTROL has been written to implement the moisture control model presented in this report. The program can compute the amount of desiccant required to maintain an acceptable dew point in the interior of a package whose design parameters have been specified by the user. In addition, interdependences among the design and storage parameters can be explored, and the internal environment of the package can be evaluated as a function of storage time. In this appendix, the overall structure, function and use of MCONTROL will be outlined.

Availability: An executable copy of the MCONTROL program is available upon request from the author:

M. R. Keenan
Sandia National Laboratories
Division 7472
P. O. Box 5800
Albuquerque, NM 87185

(505) 844-1369

Hardware: MCONTROL was designed to run on an IBM PC compatible computer with at least 256K of available memory. Since the program is computationally intensive, a math coprocessor (8087, 80287 or 80387) is required. It is also recommended that, at minimum, an IBM PC/AT class computer (80286 CPU) be used to achieve acceptable performance. MCONTROL requires a graphics adapter and monitor (CGA, EGA or VGA) with the EGA and VGA being recommended. A listing of the model parameters can be sent to a printer connected to printer port LPT1. Hard copy of the program's graphical output can be obtained with an optional Hewlett-Packard compatible plotter connected to the COM1 serial port. The plotter switch settings, in this case, must be set to 9600 baud, 8 data bits, 1 stop bit and no parity.

File System: User-defined package design models can be stored to and retrieved from a disk. The program prompts for file names, and any legal MS-DOS file name can be employed to identify the model. If, when saving a model, the named file already exists on the disk, the user is asked whether he wishes to overwrite the file or to select a new file name. All file activity is explicitly directed by the user. For example, if changes are made to the model, the model is <u>not</u> automatically rewritten to the disk.

Menu System: MCONTROL is menu-driven. Each menu consists of a vertical list of items. Selection from the menu can be made in a variety of ways. These include:

1. Pressing the listed function keys F1 through F10.

2. Highlighting the desired item using the cursor positioning keys (Home, PgUp, End, PgDn, ∧ and ∨) and typing a carriage return.

3. Typing enough of the item name to uniquely identify it and following with a carriage return.

The escape key (Esc) is used to backtrack through the menu structure.

Data Entry: MCONTROL prompts for all of the information that is required by the program and checks it for validity. The prompts can take on three different forms depending on the situation:

1. "Prompt text: " The program will accept, as a valid response to the prompt, any number or text string, as the case may be. The one limitation is that names must be less than 80 characters long.

2. "Prompt text (default response): " All model parameters have default values assigned to them. When prompted for one of these parameters, the default value is shown in parentheses. If the user wishes to accept the default response, he can simply enter a carriage return. If the default response is not acceptable, the user can type in the new value as in 1 above.

3. "Prompt text [# ... #]: " The program expects a numerical response that lies between the two numbers in brackets. If a number outside this range is entered, the user is reprompted for the inrormation.

The behavior of the program when the response in cases 1 and 3 is simply a carriage return depends on the particular data that is being requested. In most cases, a simple carriage return will cause an exit from the subfunction that is being executed. For example, when storing a model, if the response to the file name prompt is a carriage return, the Store Model routine will be aborted and the user will be returned to the main menu. In a few cases, such as when prompting for the name of a material, a carriage return will be treated as a null string and the subprogram will continue.

Several of the prompts require a single character response, for example, Y or N, yes or no. The program is insensitive to the case of the response.

Graphics: Several of the functions in MCONTROL display their results in a graphical form. Once the graph is on the screen, the program prompts for the next action. The possible responses are:

1. <cr>, a carriage return. The graph is erased and the user is returned to the menu.

2. P, typing a P invokes the plotter subroutine. This allows the graphical output to be sent to a Hewlett-Packard compatible plotter or, alternatively, to a file as a list of HPGL commands. In the latter case, the output is suitable for use by a program such as LaserPlot which recreates the graphics on a laser printer. Once the plotter routine is called, the program prompts for the plotter pen

```
╔════════ Edit Model ════════╗
║                            ║
║  F1        Title           ║
║  F2   Storage Parameters   ║
║  F3   Package Parameters   ║
║  F4   Leakage Parameters   ║
║  F5  Material Parameters   ║
║  F6  Desiccant Parameters  ║
║  ESC        Done           ║
║                            ║
╚════════════════════════════╝
```

```
╔═══ Main Menu ═══╗        ╔════════ Evaluate Model ════════╗
║                 ║        ║                                ║
║ F1  Retrieve Model       ║  F1  Pressure & Dew Pt. vs. time
║ F2   Create Model        ║  F2     Internal RH vs. time    ║
║ F3    Edit Model         ║  F3   Water Distribution (grams)║
║ F4    Save Model         ║  F4  Internal water (g) vs. time║
║ F5  Evaluate Model       ║  F5    Desiccant Dependences    ║
║ F6  Size Desiccant       ║  F6     Lifetime Dependences    ║
║ F7   Print Results       ║  F7   Max. Dew Pt. Dependences  ║
║ F8 Conversions, etc      ║  F8    Internal RH Dependences  ║
║ ESC       End            ║  F9        Re-equilibrate       ║
║                 ║        ║  ESC           Done             ║
╚═════════════════╝        ╚════════════════════════════════╝
```

```
╔════════ Conversions, etc ════════╗
║                                  ║
║  F1  P (torr) --> P(ppmv) & DP(C)║
║  F2   Dew Point (C) --> Pressure ║
║  F3  P (ppmv) --> P(torr) & DP(C)║
║  F4    P(torr) & T(C) -->  RH (%)║
║  F5    P(ppmv) & T(C) -->  RH (%)║
║  F6    RH (%) & T(C) --> Pressure║
║  F7  Dew Point & T(C) --> RH (%) ║
║  F8 RH(%) & T(C) --> Dew Point (C)║
║  F9  Saturation Pressure vs. T(C)║
║  F10   Molecular Sieve Isotherm  ║
║  ESC            Done             ║
║                                  ║
╚══════════════════════════════════╝
```

Fig. C1. Main menu and first level of sub-menus for the MCONTROL program.

```
┌═══ Desiccant Dependences ═┐          ┌═══ Lifetime Dependences ═┐
│                           │          │                          │
│  F1   Storage Temperature │          │  F1   Storage Temperature│
│  F2        Storage RH     │          │  F2        Storage RH    │
│  F3    Maximum Dew Point  │          │  F3    Maximum Dew Point  │
│  F4   Maximum Internal RH │          │  F4   Maximum Internal RH │
│  F5     Helium Leak Rate  │          │  F5     Helium Leak Rate  │
│  F6      Design Lifetime  │          │  F6      Desiccant Size   │
│  F7  Variable Temperature │          │  F7  Variable Temperature │
│  ESC         Done         │          │  ESC         Done         │
│                           │          │                          │
└───────────────────────────┘          └──────────────────────────┘

              ┌════════ Evaluate Model ═══════┐
              │                               │
              │  F1  Pressure & Dew Pt. vs. time │
              │  F2       Internal RH vs. time   │
              │  F3    Water Distribution (grams)│
              │  F4  Internal water (g) vs. time │
              │  F5       Desiccant Dependences  │
              │  F6       Lifetime Dependences   │
              │  F7     Max. Dew Pt. Dependences │
              │  F8     Internal RH Dependences  │
              │  F9          Re-equilibrate      │
              │  ESC            Done             │
              │                               │
              └───────────────────────────────┘

┌═ Internal RH Dependences ═┐          ┌═ Max. Dew Pt. Depencences ═┐
│                           │          │                            │
│  F1    Storage Temperature│          │  F1    Storage Temperature │
│  F2         Storage RH    │          │  F2         Storage RH     │
│  F3      Desiccant Size   │          │  F3      Desiccant Size    │
│  F4    Maximum Dew Point  │          │  F4    Maximum Internal RH │
│  F5     Helium Leak Rate  │          │  F5     Helium Leak Rate   │
│  F6      Design Lifetime  │          │  F6      Design Lifetime   │
│  F7   Variable Temperature│          │  F7   Variable Temperature │
│  ESC         Done         │          │  ESC         Done          │
│                           │          │                            │
└───────────────────────────┘          └────────────────────────────┘
```

Fig. C2. Evaluate Model menu of the MCONTROL program and related sub-menus showing the model parameter interrelationships that can be investigated.

```
┌──────── Edit Model ════════┐
│                            │
│   F1        Title          │
│   F2    Storage Parameters │
│   F3    Package Parameters │
│   F4    Leakage Parameters │
│   F5   Material Parameters │
│   F6   Desiccant Parameters│
│   ESC          Done        │
│                            │
└────────────────────────────┘
```

Storage Parameters   Leakage Parameters

Temperature   Helium Leak Rate
Relative Humidity
Design Lifetime   Miscellaneous Water
Max. Internal Dew Point
Lower Use Temperature   Number of O-ring seals
Upper Use Temperature   Name for Each Seal
                                            Permeabilities
                                         Activation Energies
Package Parameters   O-ring Circumferences
                                         Sealing Compressions
Free Volume
Free Surface Area   Number of Planar Barriers
Temperature When Sealed   Name for Each Barrier
Humidity When Sealed   Permeabilities
                                         Activation Energies
                                            Barrier Areas
Material Parameters   Barrier Thicknesses

Number of Henry's Law Materials
Name of Each Material   Desiccant Parameters
Mass of Each Material
Saturation Absorptions   Type of Molecular Sieve
Equilibration Humidities   Mass of Desiccant
                                         Sieve Capacity Lost in Assembly

   Fig. C3. Parameters incorporated into the packaging design model implemented
by the MCONTROL program. The break down of these parameters into the groups
used by the Edit Model function are also shown.

```

speed (paper or transparency) or for the name of the file to receive the HPGL commands.

3. F, typing an F causes the numerical data to be stored in an ASCII file. This allows the user to peruse the actual plotted data at a later time or to import the data into another program such as a spreadsheet. The first line in the file consists of 2 entries. The first is the number of lines of data and this followed by the number of data entries on each line. The rest of the file consists of the data with an X-Y pair of numbers on each line (if 2 curves are plotted, the format is $X_1$ $Y_1$ $X_2$ $Y_2$).

## MCONTROL: Structure and Function

The overall structure of the MCONTROL program and the menu hierarchy are illustrated in Figs. C1 - C3. The list below briefly describes the function of each of the menu selections.

Main Menu: this menu is displayed when the MCONTROL program is invoked.

1. Retrieve Model -- loads a package design model into the program from disk storage. The user is prompted for the name of the disk file that contains the model.

2. Create Model -- allows the user to create a package design model. The user is prompted for all of the design parameters that are described below.

3. Edit Model -- calls up the Edit menu which allows the user to make selective changes to the design model.

4. Save Model -- stores the package design model to a disk file. The user is prompted for the file name.

5. Evaluate Model -- calls up the Evaluate menu which allows the user to examine the interdependences between the various design and storage parameters.

6. Size Desiccant -- computes, based on the design model, the amount of desiccant required to maintain an acceptable dew point within a package. Three quantities are calculated. The first is the amount of desiccant needed to keep the package from exceeding its maximum dew point requirement during isothermal storage. The second is the amount required to maintain the dew point below the lower use temperature. The third is the amount of desiccant needed to keep the dew point below the specified maximum during a temporary excursion to the upper use temperature.

7. Print Results -- the design model and computed results are printed to the screen or to an attached printer as desired by the user.

8.  Conversions, etc -- calls up the conversions menu.  This allows the user to readily convert moisture content units among pressures, dew points and humidities.

9.  End -- this causes the program to exit.  The user is asked to verify that he wishes to quit and is further asked if the package design model is to be saved.

Edit Menu:  This menu is called from the main menu and allows the user to make changes to the model.  The user selects from the menu the group of parameters that he wishes to alter.  The information stored in each parameter group is detailed below.  Within a group, the user is prompted for each piece of information.  If the particular item requires no change, the user should respond to the prompt with a simple carriage return to accept the default value.  The parameter groups and menu choices are:

1.  Title -- title given to the model

2.  Storage Parameters

3.  Package Parameters

4.  Leakage Parameters

5.  Material Parameters

6.  Desiccant Parameters

7.  Done -- returns the user to the main menu

Evaluate Menu:  is called from the main menu.  In general, this should only be invoked after the proper desiccant size has been computed.  The menu choices are:

1.  Pressure and Dew Point vs time -- computes and plots the water vapor partial pressure and dew point inside the package as a function of storage time.

2.  Internal RH vs time -- graphs the package's internal relative humidity as a function of storage time.

3.  Water Distribution (grams) -- Displays how the water within a package is distributed (in the atmosphere, materials, desiccant, etc.) during storage.

4.  Internal water (g) vs time -- computes the total water contained in the package as a function of storage time.

5.  Desiccant Dependences -- calls up the Desiccant Dependences menu which allows the user to evaluate the manner in which the amount of desiccant required to maintain the specified maximum dew point varies with:

    a.  Isothermal storage temperature
    b.  Isobaric storage relative humidity
    c.  Maximum dew point specification
    d.  Maximum internal relative humidity
    e.  Helium leak rate
    f.  Design lifetime of the package
    g.  A sinusoidally varying storage temperature

6.  Lifetime Dependences -- invokes the <u>Lifetime Dependences</u> menu.  This permits the lifetime of the package, defined as the time required to achieve the maximum allowable dew point, to be computed as a function of:

    a.  Isothermal storage temperature
    b.  Isobaric storage relative humidity
    c.  Maximum dew point specification
    d.  Maximum internal relative humidity
    e.  Helium leak rate
    f.  Mass of desiccant contained in the package
    g.  A sinusoidally varying storage temperature

7.  Maximum Dew Point Dependences -- calls the <u>Max. Dew Pt. Dependences</u> menu which evaluates how the dew point at the end of the design life varies with:

    a.  Isothermal storage temperature
    b.  Isobaric storage relative humidity
    c.  Mass of desiccant contained in the package
    d.  Maximum internal relative humidity
    e.  Helium leak rate
    f.  Design lifetime of the package
    g.  A sinusoidally varying storage temperature

8.  Internal RH Dependences -- calls up the <u>Internal RH Dependences</u> menu which computes the relative humidity inside the package at the end of its design life as a function of:

    a.  Isothermal storage temperature
    b.  Isobaric storage relative humidity
    c.  Maximum dew point specification
    d.  Mass of desiccant contained in the package
    e.  Helium leak rate
    f.  Design lifetime of the package
    g.  A sinusoidally varying storage temperature

9.  Re-equilibrate -- computes the water vapor partial pressure and dew point inside a package during a temporary jump to an elevated temperature that is specified by the user.  The results are given as a function of the isothermal storage time prior to the jump.

10. Done -- returns the user to the main menu

<u>Conversions Menu</u>:  the various conversions that can be performed are self--
         explanatory.  These include:

1.  Pressure (torr) to Pressure (ppmv) and Dew Point (°C)

2.  Dew Point (°C) to Pressure (torr and ppmv)

3.  Pressure (ppmv) to P (torr) and Dew Point (°C)

4.  Pressure (torr) and Temperature (°C) to RH (%)

5.  Pressure (ppmv) and Temperature (°C) to RH (%)

6.  RH (%) and Temperature (°C) to Pressure (torr and ppmv)

7.  Dew Point (°C) and Temperature (°C) to RH (%)

8.  RH (%) and Temperature (°C) to Dew Point (°C)

9.  Saturation Pressure vs Temperature (°C) -- plots the saturation water
    vapor pressure as a function of temperature

10. Molecular Sieve Isotherm -- displays the equilibrium adsorption of
    water by molecular sieves as a function of water vapor pressure

11. Returns the user to the main menu


## MCONTROL: Model Parameters

     The package design parameters required by the MCONTROL model are listed in
Fig. C3.  A brief description of each along with the default values are given
below.

<u>Storage Parameters</u>:

1.  Storage temperature (25°C) -- isothermal storage temperature.  In the
    case of the sinusoidally variable temperature, this represents the
    average temperature.

2.   Storage Humidity (50%) -- relative humidity in the external storage
    environment.

3.  Design life (20 years) -- period of time over which we wish to control
    the moisture level.

4.  Maximum dew point (-20°C) -- desiccant will be sized so that this dew
    point will not be exceed over the duration of the design life.

5.  Lower use temperature (-48°C - -55°F) -- when sizing the desiccant,
    the amount required to maintain this dew point will also be computed.

6. Upper use temperature (74°C - 165°F) -- desiccant required to maintain the maximum dew point during a temporary jump to this temperature will be computed.

Package Parameters:

1. Free volume (1000 cm$^3$) -- free volume within the package.

2. Free surface (600 cm$^2$) -- area of free surface within the package.

3. Sealing temperature (25°C) -- environmental temperature at the time the package was sealed.

4. Sealing humidity (50%) -- relative humidity at the time of sealing.

Henry's Law Material Parameters:

Number of absorbing materials (0) -- this is the number of organic materials contained within a package that absorb water according to Henry's law. The program is limited to 10 such materials. Each material is characterized by:

    a. name of the material
    b. mass of the material contained in the package in grams
    c. saturation (100% RH) water uptake by the material in % w/w
    d. humidity at which the material was equilibrated before sealing

Desiccant Parameters:

1. Type (4A) -- type of desiccant from the choice of 3A, 4A and molded.

2. Mass (0) -- mass of desiccant in grams incorporated into the package.

3. Lost capacity (0) -- capacity of the molecular sieve desiccant that was used up during the assembly of the package in % w/w

Leakage Parameters:

1. Helium leak rate (1 × 10$^{-6}$ std cc/sec) -- leak rate of the package in the absence of permeation.

2. Miscellaneous water (0) -- grams of water that enter the package through processes such as transient permeation and chemical reactions.

3. Number of o-rings (0) -- the number of o-ring seals incorporated into the package. This is limited to 10 different materials. For each o-ring, the following information is required:

    a. a description of the o-ring
    b. the permeability coefficient at 25°C
    c. the activation energy for permeation (8 kcal/mole)
    d. the circumferential length of the o-ring in cm
    e. compressive strain used to form the seal (25%)

4. Number of other permeable barriers (0) -- the number of additional permeable barriers through which permeation takes place. The number of barriers is limited to 10 different materials and the assumption of 1-dimensional diffusion through a plane will be made. The required pieces of information about each of these barrier materials are:

    a. a description of the barrier
    b. the permeability coefficient of the barrier at 25°C
    c. the activation energy for permeation (8 kcal/mole)
    d. exposed surface area of the barrier in $cm^2$
    e. thickness of the barrier in cm

## APPENDIX D: POLYMER PERMEABILITIES

Successful implementation of the moisture control strategy described in this report requires that reasonable values for certain polymeric material properties be known. These include the water vapor permeabilities of seal and barrier materials, and the solubilities of water in a package's internal organic constituents. Compilations of such data (mostly permeabilities) are given for a variety of materials in Refs. 14 and 26-29. Using primarily these sources, I have put together the lists below to serve as a ready reference to polymer permeability. It must be cautioned, however, that these permeability values are attended by relatively large uncertainties, factors of two are not uncommon. Water vapor permeabilities are notoriously difficult to measure and different experimental methods often yield differing results for the same material. In addition, permeabilities may vary significantly with the manner in which a given material is formulated and processed. If very precise permeability values are required, they should be measured for the particular materials of interest. For the purposes of material selection and assessing the moisture control problem, however, literature permeability values provide a useful guide. In many cases, factors of two uncertainty are unimportant compared to the five orders of magnitude range of permeabilities exhibited by common polymers.

Solubilities of water in polymers have not been included in this appendix for a number of reasons. Most materials that absorb large quantities of water do not follow Henry's law, thus, the absorption isotherm cannot be described by a single number. As a result, compilations of solubilities are not as prevalent as those of permeabilities. In addition, much of the solubility data in the literature is misleading. Often, especially in manufacturers' literature, solubility is expressed in terms of the mass of water absorbed in 24 hrs. Unfortunately, most materials will not reach saturation within that period of time, and the fraction of saturation that they do achieve will vary greatly with the diffusion coefficient of the material. In contrast to permeability, solubility can be easily and inexpensively measured[17] and this is the approach to estimating solubility that is recommended.

### Elastomers: O-ring formulations[26]

| Parker Seal Co. Compound | Material | Permeability (25°C) std cc/(cm·sec·torr) | E kcal/mole |
|---|---|---|---|
| Silicone S604-70 | Organosiloxane | $1.9 \times 10^{-7}$ | -2.2 |
| Fluorosilicone L677-70 | Fluorinated Silicone | $1.3 \times 10^{-7}$ | -0.8 |
| PNF F953-70 | Phosphonitrilic Fluoroelastomer | $1.1 \times 10^{-7}$ | 0.0 |
| Nitrile N304-75 | Random Acrylonitrile/ Butadiene Copolymer | $5.7 \times 10^{-8}$ | 2.3 |
| Hypalon H723-65 | Chlorosulfonated Polyethylene | $1.0 \times 10^{-8}$ | 2.4 |
| Neoprene C873-70 | Polychloroprene | $8.7 \times 10^{-9}$ | 2.3 |
| Viton V747-75 | Vinylidene Fluoride/ Hexafluoropropylene | $5.7 \times 10^{-9}$ | 4.0 |
| EPR E515-80 | Ethylene/Propylene | $4.8 \times 10^{-9}$ | 4.7 |
| Butyl B612-70 | Isobutylene/Isoprene | $6.1 \times 10^{-10}$ | --- |

## Molding Compounds[27]

| Resin | Filler | Permeability (25°C) std cc/(cm·sec·torr) |
|-------|--------|------------------------------------------|
| Silicone | Glass Fiber + Silica | $2.4 \times 10^{-8}$ |
| Polyester SMC | Glass Fiber | $2.3 \times 10^{-8}$ |
| Phenolic | Glass Fiber | $1.1 \times 10^{-8}$ |
| DAP | Glass Fiber | $4.5 \times 10^{-9}$ |
| Epoxy | Glass Fiber + Mineral | $2.9 \times 10^{-9}$ |

## Miscellaneous Polymers

| Material | Permeability (25°C) std cc/(cm·sec·torr) | E kcal/mole | Reference |
|----------|------------------------------------------|-------------|-----------|
| Polyphenylene oxide | $4.1 \times 10^{-8}$ | -- | 29 |
| Polyurethane elastomer | $3.1 \times 10^{-8}$ | -- | 30 |
| Polyisoprene (natural rubber) | $2.3 \times 10^{-8}$ | -- | 28 |
| ABS | $2.1 \times 10^{-8}$ | -- | 27 |
| Polymethylmethacrylate (Lucite) | $1.5 \times 10^{-8}$ | -- | 27 |
| Polycarbonate (Lexan) | $1.4 \times 10^{-8}$ | -- | 28 |
| Nylon 6/6 | $1.3 \times 10^{-8}$ | -- | 27 |
| Polystyrene | $8.4 \times 10^{-9}$ | 0 | 28 |
| Polyimide (Kapton) | $5 \times 10^{-9}$ | 0 | 32 |
| Polyacrylonitrile | $3.0 \times 10^{-9}$ | -- | 28 |
| Epoxy (unfilled) | $2.5 \times 10^{-9}$ (40°C) | -- | 22 |
| Polyester (Mylar) | $1.8 \times 10^{-9}$ | 0.5 | 28 |
| Polytetrafluoroethylene (Teflon) | $1 \times 10^{-9}$ | -- | 27 |
| Polyethylene ($\rho$=0.922) | $9 \times 10^{-10}$ | 8 | 14 |
| Polypropylene ($\rho$=0.907) | $5.1 \times 10^{-10}$ | 10 | 14 |
| Teflon FEP | $3 \times 10^{-10}$ | 4.7 | 31 |
| Polyvinylidene chloride (Saran) | $5 \times 10^{-12}$ | 11.0 | 28 |



Fig. D1. Correlation between the permeabilities of polymers to water and their activation energies for permeation.

$$E = -2.8\log(Q) - 19.9$$

Often, the activation energy for permeation is either not known or not available. In Fig. D1, the activation energy is plotted against the permeation coefficient for each of the materials that have both values given above. While there is a lot of scatter in the data, a clear trend emerges. In general, materials that have low room temperature permeabilities tend to have relatively higher activation energies. This trend can be used (cautiously!) to estimate the activation energy for permeation in cases where it is not known.

DISTRIBUTION:

AFATL/MNF  (2)
Attn:  R. Mabry
       Steve Smith
Eglin AFB, FL 32542

Allied-Signal Aerospace Co.  (4)
Kansas City Division
Attn:  C. R. Baxter, D/343
       A. W. Gordon, D/842
       G. R. Lenox, D/818
       R. S. Sanders, D/837
P. O. Box 419159
Kansas City, MO 64141

General Electric Company  (1)
Neutron Devices Department
Attn:  C. W. Jones
P. O. Box 2908
Largo, FL 34294

Los Alamos National Laboratory  (2)
Attn:  James Hayden, WX-1, MS C936
       G. W. Taylor, M-1, MS C920
Los Alamos, NM 87545

| | | |
|---|---|---|
| 1513 | D. W. | Larson |
| 1521 | S. N. | Burchett |
| 1800 | R. J. | Egan |
| 1810 | D. W. | Schaefer |
| 1811 | R. L. | Clough |
| 1811 | L. R. | Gilliom |
| 1812 | K. T. | Gillen |
| 1812 | C. L. | Renschler |
| 1813 | J. G. | Curro |
| 1813 | P. F. | Green |
| 1813 | P. B. | Rand |
| 1815 | G. E. | Pike |
| 1820 | J. B. | Woodard |
| 1823 | J. A. | Borders |
| 1832 | W. B. | Jones |
| 1833 | J. L. | Jellison |
| 1834 | A. K. | Hays |
| 1834 | M. C. | Oborny |
| 2134 | D. W. | Palmer |
| 2311 | T. D. | Donham |
| 2312 | D. J. | Allen |
| 2313 | A. E. | Verado |
| 2314 | R. F. | Rieden |
| 2315 | M. J. | Smartt |
| 2321 | E. F. | Hartman |
| 2322 | G. J. | Scrivner |
| 2331 | A. E. | Sill |

| | | |
|---|---|---|
| 2334 | G. M. | Heck |
| 2334 | F. J. | Peter |
| 2335 | H. M. | Witek |
| 2336 | E. J. | Nava |
| 2337 | L. J. | Dalton |
| 2341 | C. R. | Alls |
| 2341 | M. L. | Young |
| 2342 | D. W. | Arquette |
| 2343 | W. H. | Schaedla |
| 2344 | C. S. | Williams |
| 2345 | B. C. | Walker |
| 2346 | R. L. | O'Nan |
| 2361 | T. J. | Williams |
| 2361 | G. E. | Clark |
| 2362 | M. B. | Murphy |
| 2364 | J. F. | Jones, Jr. |
| 2364 | A. J. | Medina |
| 2512 | J. G. | Harlan |
| 2513 | D. E. | Mitchell |
| 2514 | L. L. | Bonzon |
| 2515 | P. D. | Wilcox |
| 2522 | R. P. | Clark |
| 2523 | J. Q. | Searcy |
| 2525 | R. B. | Diegle |
| 2526 | N. J. | Magnani, Actg. |
| 2531 | W. D. | Williams |
| 2532 | J. J. | Marron |
| 2533 | G. R. | Laguna |
| 2534 | H. M. | Bivens |
| 2541 | S. B. | Martin |
| 2542 | J. P. | Abbin |
| 2543 | K. G. | McCaughey |
| 2545 | J. H. | Barnette |
| 2551 | D. E. | Carnicom |
| 2552 | D. H. | Weingarten |
| 2553 | J. O. | Harris |
| 2561 | R. A. | Damerow |
| 2564 | F. M. | Bacon |
| 2565 | J. A. | Wilder |
| 3141 | S. A. | Landenberger (5) |
| 3141-1 | C. L. | Ward (8) for DOE/TIC |
| 3151 | W. I. | Klein  (3) |
| 5111 | D. N. | Bray |
| 5113 | R. W. | Jorgensen |
| 5113 | W. J. | Dalby |
| 5114 | W. D. | Ulrich |
| 5122 | J. N. | Baker |
| 5126 | W. D. | Chadwick |
| 5127 | M. J. | Eaton |
| 5128 | B. E. | Bader |
| 5131 | G. N. | Beeler, Actg. |
| 5132 | D. M. | McCall |

| | | | | |
|---|---|---|---|---|
| 5132 | M. M. Plugge | 8174 | J. W. Hickman, Actg. |
| 5132 | S. D. Meyer | 8310 | R. W. Rhode |
| 5133 | G. H. Whiting | 8313 | R. W. Bradshaw |
| 5141 | C. A. Harris | 8316 | J. E. Costa |
| 5143 | R. D. Robinett | 8316 | R. E. Gott |
| 5144 | D. E. Ryerson | 8316 | R. E. Stoltz |
| 5145 | D. H. Schroeder | 8524 | J. A. Wackerly |
| 5147 | G. L. Maxam | 9121 | L. T. James |
| 5151 | W. C. Nickell | 9122 | R. H. Braasch |
| 5153 | S. L. Jeffers | 9123 | J. M. Holovka |
| 5153 | J. J. Lang | 9127 | D. D. Dell |
| 5154 | R. L. Alvis | 9127 | I. K. Evans |
| 5161 | D. F. McVey | 9127 | C. E. Olson |
| 5165 | J. M. Freedman | 9127 | V. C. Rimkus |
| 5166 | R. C. Hartwig | | |
| 5171 | E. A. Chipman | | |
| 5172 | R. F. Glaser | | |
| 5173 | P. D. Merillat | | |
| 5175 | A. E. Sill | | |
| 5176 | R. E. Trellue | | |
| 7234 | R. J. Martinez | | |
| 7252 | D. W. Bushmire | | |
| 7400 | W. E. Alzheimer | | |
| 7410 | T. J. Young | | |
| 7413 | G. L. Cessac | | |
| 7413 | M. D. Lucas | | |
| 7470 | J. L. Ledman | | |
| 7471 | L. E. Pope | | |
| 7472 | T. R. Guess | | |
| 7472 | M. R. Keenan (50) | | |
| 7472 | R. L. Myers | | |
| 7472 | P. J. Nigrey | | |
| 7472 | A. E. Smith | | |
| 7472 | K. B. Wischmann | | |
| 7473 | J. W. Munford | | |
| 7476 | F. P. Gerstle | | |
| 7480 | J. K. S. Walter, Jr. | | |
| 7484 | W. R. Leuenberger | | |
| 7551 | J. W. Guthrie | | |
| 8131 | W. R. Bolton | | |
| 8132 | A. S. Rivenes | | |
| 8133 | A. C. Skinrood | | |
| 8134 | M. H. Rogers | | |
| 8154 | D. J. Havlik | | |
| 8155 | R. G. Miller | | |
| 8156 | M. E. John | | |
| 8161 | M. H. Reynolds | | |
| 8162 | C. T. Yokomizo | | |
| 8163 | W. G. Wilson | | |
| 8164 | P. G. Heppner | | |
| 8165 | G. C. Story | | |
| 8171 | C. B. Layne | | |
| 8172 | R. J. Gallagher | | |
| 8173 | L. D. Brandt | | |